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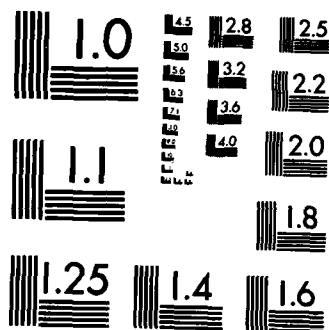
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# NAVAL POSTGRADUATE SCHOOL

## Monterey, California



# THESIS

THE EFFECTS OF GRAIN SIZE ON THE  
MARTENSITIC TRANSFORMATION IN  
COPPER-ZINC-ALUMINUM SHAPE MEMORY ALLOYS

by

Timothy James Gann

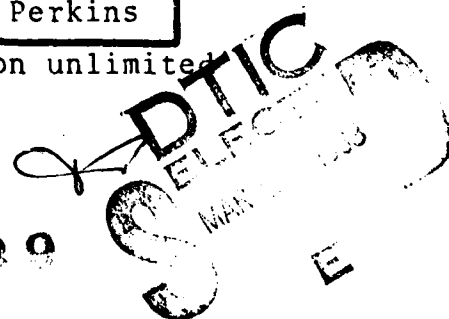
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The Effects of Grain Size on the Martensitic  
Transformation in Copper-Zinc-Aluminum  
Shape Memory Alloys

by

Timothy James Gann  
Lieutenant, United States Navy  
B. S., Purdue University, 1975

Submitted in partial fulfillment of the  
requirements for the degree of

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from the

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# ABSTRACT

The effect of grain size on the martensitic transition in a Cu-Zn-Al alloy was studied. As grain size increases the martensite phase is stabilized relative to the parent phase, as indicated by an increase in the martensite start temperature ( $M_s$ ). Martensite stabilization due to thermal cycling is also corroborated. A method of grain refinement is introduced which will consistently yield grain sizes of less than 0.1 millimeters.

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## I. INTRODUCTION

Recently, much attention has been given to a number of alloys which exhibit a property known as Shape Memory Effect (SME). These alloys are able to sustain large amounts of deformation and then, upon unloading or thermal treatment, revert back to their original shape. This phenomenon has been observed in a number of alloys, both binary (Nickel-Titanium) and tertiary (Copper-Zinc-Aluminum).

The research devoted to these alloys has not been confined to purely metallurgical study but includes the development of their practical application as engineering materials. As reported by Wayman [Ref. 1], items such as pipe couplings, seals, clamps, thermo-mechanical actuators and several prototype heat engines are now in production or nearly so. In the medical arts these alloys are being exploited for their SME properties as orthodontic appliances, intercranial aneurism clamps and for orthopedic devices.

The shape memory effect is a direct result of thermo-elastic martensitic transformation. Unlike steels, which also undergo martensitic transformation, a shape memory alloy transforms to martensitic by forming plates which grow in a continuous manner as temperature is decreased. As the temperature is raised the plates revert back to the

parent phase in an exact reversal of the original transformation. In most shape memory alloys there is only one crystallographic route back to the parent phase while there are several thermal or stress related routes to induce the formation of martensite. Therefore, when one of these alloys is deformed while in its martensitic phase, it will regain its original shape when heated to a temperature above that required for complete transformation to the parent phase ( $A_f$ ). This process is illustrated in Figure 1.1, taken from [Re 2]. This SME phenomenon is due to the nearly exact reconstruction of the original parent atomic crystal.

One family of shape memory alloys with great potential for practical application is that based on the tertiary Copper-Zinc-Aluminum (Cu-Zn-Al) alloy system. These alloys are typically about 70 wt.% copper brass with the addition of aluminum on the order of 2-8 wt.%. The advantages of the Cu-Zn-Al alloys are found in their relatively low cost, ease of fabrication and the availability of a useful range of martensite transformation temperatures attainable by alloy concentration variations. The significant reaction is the transformation of the ordered body centered cubic (BCC) beta phase to a close packed thermoelastic martensite structure.

There are several other characteristics of the beta-to-martensite phase transformation which are of interest.

Given a particular composition, how may the martensitic start temperature ( $M_s$ ) be influenced by variation of dislocation density through cold work, by prior thermomechanical processing or by variation of grain size?

A significant disadvantage of Cu-Zn-Al alloys is their poor resistance to fatigue failure owing, in part, to their inherently large grained microstructure. In the past attempts to control grain size in this alloy have taken several different approaches. One method involves the addition of a fourth element in an effort to provide more beta phase nucleation sites. Another approach has been to carefully control the temperature and time of solution treatment to encourage the retention of a small amount of the alpha phase just prior to quench, with the presence of this second phase intended to stifle grain growth of the parent beta phase. Another method will be introduced in this study.

The purpose of this study was to determine the effect of grain size on the  $M_s$  temperature. By subjecting normalized specimens of a specific alloy to various thermal and thermomechanical treatments a range of grain sizes was obtained. These samples were examined by differential scanning calorimetry and the  $M_s$  temperatures were obtained.

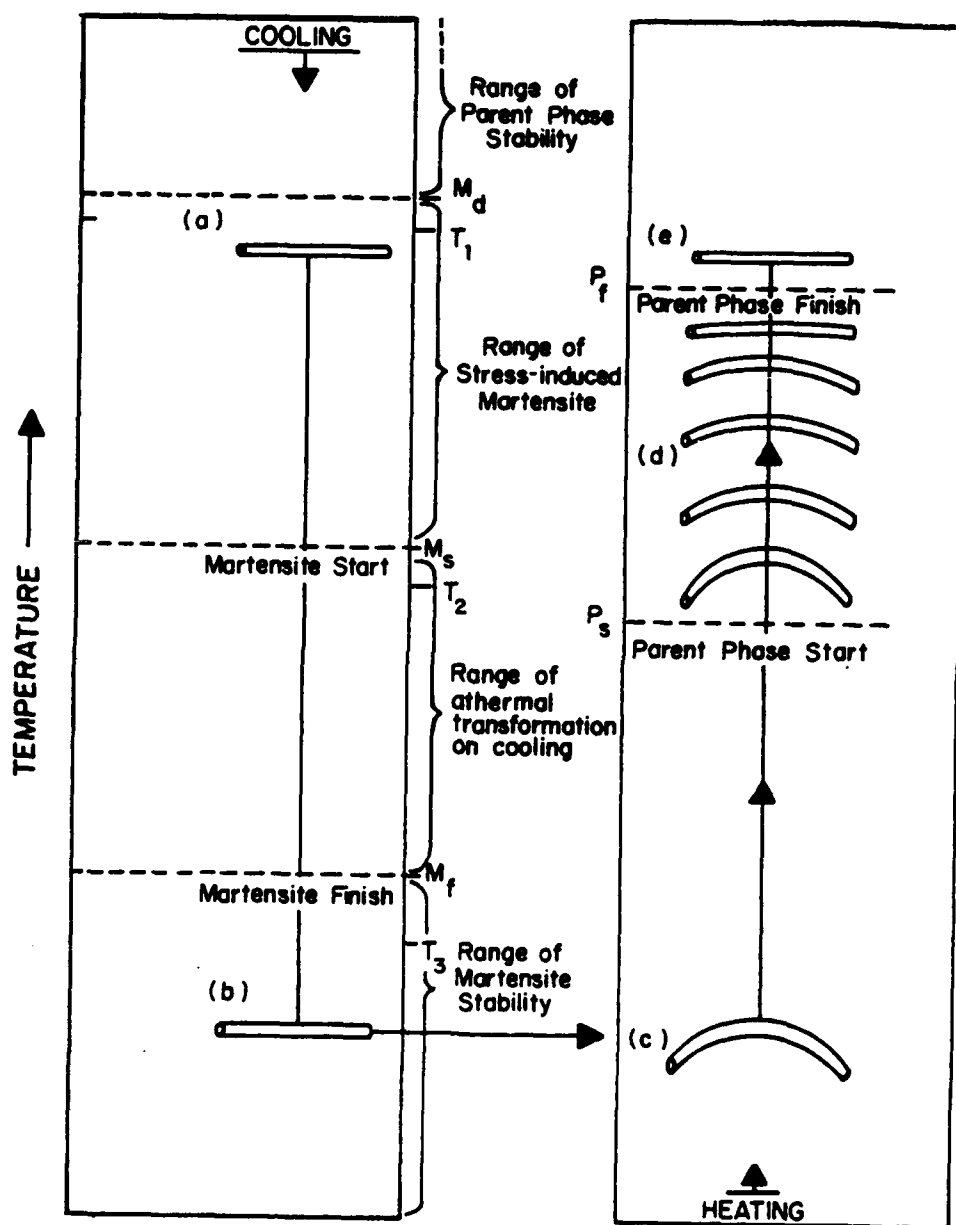


Figure 1.1 Schematic Diagram of the Shape Memory Effect (SME)

## II. EXPERIMENTAL PROCEDURE

### A. ALLOY PREPARATION

The Cu-Zn-Al alloy studied was provided by Delta Materials Research Limited, Ipswich, Suffolk, England. Alloy designator B was used exclusively for this research. Its nominal composition is 76 w/o Cu, 16.5 w/o Zn, and 7.5 w/o Al. Alloy B was selected on the basis of its reputed  $M_s$  temperature, which would place it in the martensite phase at room temperature. The as-received material was machined into rod-shaped test specimens 2.25 inches (57.15 mm) in length and 0.138 inches (3.5 mm) in diameter. In order to homogenize the specimens, they were sealed in evacuated quartz tubes, solution treated and quenched. The solution temperature was determined by phase diagrams contained in INCRA Research Report Number 78R1, [Ref. 3]. The specimens were annealed at 723 deg. C for 20 minutes and then water quenched. Subsequent microscopic examination revealed a homogeneous martensitic microstructure with a nominal grain diameter of about .3 mm. Each specimen was hand polished followed by electropolishing in a 10% KCN solution (6 V.a.c. for 30 seconds).

### B. BETA PHASE SOLVUS DETERMINATION

One of the homogenized rods was cut into short lengths to be used in determination of the beta phase solvus



temperature. An approximate value of this quantity was obtained from the phase diagram of [Ref. 3]. Each of the specimens was heat treated at a higher temperature than its predecessor and subsequently water quenched. This incremental heat treatment process was started at 823 deg. K and increased by 5 deg. K for each subsequent specimen. The solvus temperature was determined when, upon microscopic examination, the entire microstructure of the specimen had transformed to martensite. The beta phase solvus for alloy B was found to be 843 deg. K which was in approximate agreement with the phase diagram of [Ref. 3].

#### C. GRAIN REFINEMENT

Due to the nature of this study the method of grain refinement chosen had to be one which would produce minimal extraneous effects on the  $M_s$  temperature. Variables such as temperature, time at temperature and overall thermal history are all factors affecting grain size, but may also alter  $M_s$  temperature in and of themselves. In the search for a method of grain refinement which would meet the requirements of this study two ideas were found in the related literature.

The first of these methods was developed by Enami, et. al., [Ref. 4], and involves the addition of vanadium to the Cu-Zn-Al alloy. This addition is accomplished by remelting alloy samples in a vacuum and adding different amounts of

vanadium. Although no significant difference in shape memory behavior was noted there were other important alterations of morphology, such as the precipitation of a vanadium rich V-Al phase, which could influence the beta-to-martensite transition. This method was, therefore, considered not to be a viable option for this study.

The second of the grain refinement methods was proposed in a paper by J. M. Cook, et. al., [Ref. 5]. Specimens were heat treated to a temperature just within the single phase region and then water quenched. By careful control of solution treatment temperature and time, various amounts of the alpha phase is retained as fine Widmanstatten plates in the martensite structure. The presence of the alpha phase acts to inhibit rapid grain growth. The presence of this second phase, however, was considered undersirable for this study.

The production of specimens of alloy B with grain sizes from 0.2 to 1.0 millimeters was found to be easily obtainable by varying the solution treatment temperature from the solvus temperature to approximately 50 degrees below the melting temperature. Accordingly, six specimens were solution treated from the normalized state and then water quenched to produce the resultant grain sizes listed in Table I.

TABLE I  
Solution Treatment Temperature and Grain Size

| Solution Temperature<br>(Deg. K) | Grain Size<br>(mm) |
|----------------------------------|--------------------|
| 873                              | 0.21               |
| 977                              | 0.38               |
| 1073                             | 0.53               |
| 1133                             | 0.63               |
| 1148                             | 0.83               |
| 1173                             | 1.01               |

The smallest grain sizes obtained were produced by a duplex treatment involving deformation. After initial immersion of a normalized sample in molten salt at 550 deg. C, as the temperature of the specimen approach 493 deg. K, it was deformed approximately 70 percent. The specimen was allowed to continue heating, during the after deformation, to the solution temperature of 848 deg. K, whereupon it was immediately water quenched. In order to carry out this operation, a pair of locking pliers was modified by grinding the jaws flat and imbedding a thermocouple into the tip of one of the jaws. By connecting the thermocouple to a Newport pyrometer the actual temperature of the specimen could be monitored and deformation induced while the specimen was submerged in the molten salt. This process yielded a grain size of 0.08 millimeters and was found to be very repeatable in terms of producing grain sizes consistently less than 0.1 millimeters.

Each of the specimens was then polished, etched and photographed. The Heyn method of grain sizing was then employed to determine grain diameter. Micrographs of each grain size obtained, configured with the random lines of the grain sizing method, are shown in Figures 2.1 to 2.7.

#### D. DIFFERENTIAL SCANNING CALORIMETRY

A small section of 40 to 60 milligrams of each of the different grain size specimens was thermally cycled in a Perkin-Elmer DSC-2. The DSC measures changes in the power required to maintain a sample and sample holder at the same temperature as a reference holder. Transformation from the beta phase to martensite is exothermic while the reverse transformation, from martensite back to the parent phase, is endothermic. Start and finish temperatures of these reactions are recorded on the chart abscissa. The DSC was programmed to cycle from 260 to 520 deg. K on the first cycle and from 260 to 360 deg. K on subsequent cycles for each specimen. A slow heating and cooling rate of 10 deg. K per minute was chosen to ensure thorough transformation during cycling and to allow easy data reduction from the strip chart recordings.  $M_s$  was determined from the strip chart by the point of departure of the exothermic curve from the relatively straight line produced by the DSC cooling energy. An illustration of the heating and cooling curves produced is given by Figure 2.8.

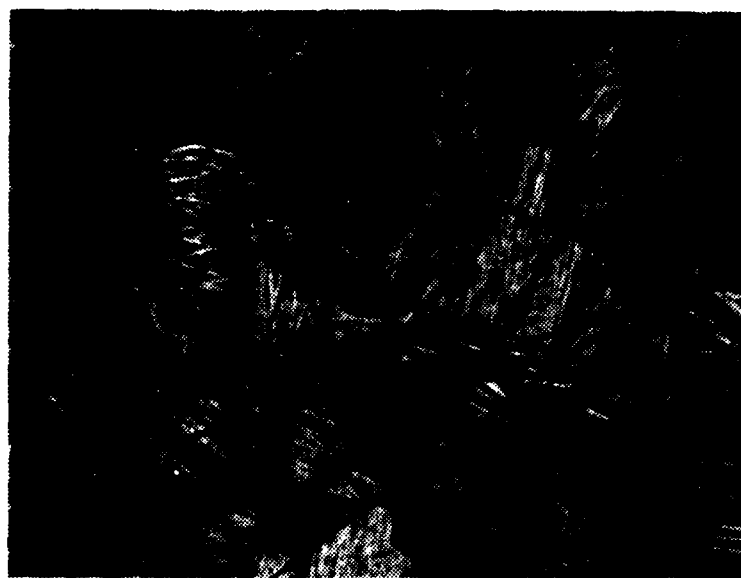


Figure 2.1 Specimen of Grain Size of 0.08 (mm). (100x)



Figure 2.2 Specimen of Grain Size of 0.21 (mm). (100x)



Figure 2.3 Specimen of Grain Size of 0.38 (mm). (50x)



Figure 2.4 Specimen of Grain Size of 0.53 (mm). (50x)



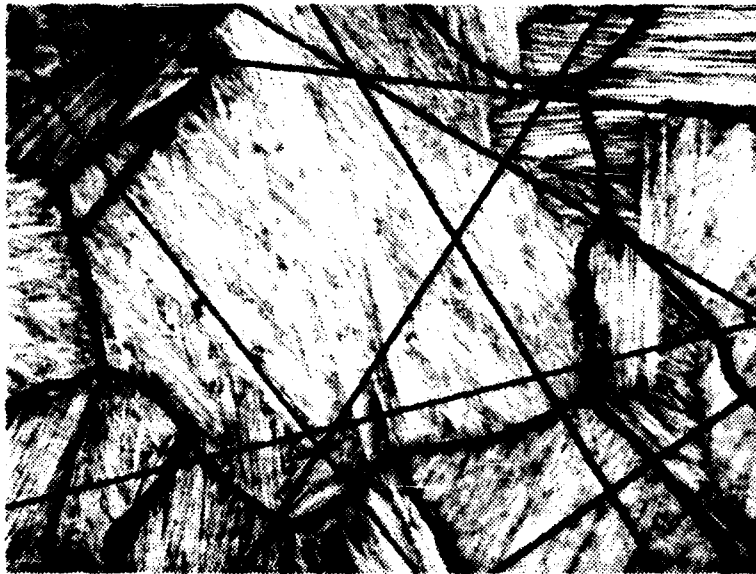


Figure 2.5 Specimen of Grain Size of 0.63 (mm). (50x)



Figure 2.6 Specimen of Grain Size of 0.83 (mm). (50x)

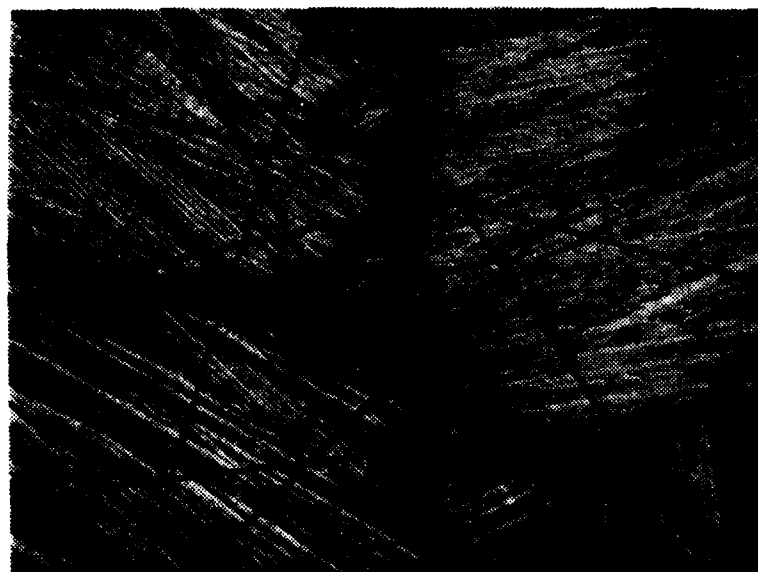


Figure 2.7 Specimen of Grain Size of 1.01 (mm). (50x)

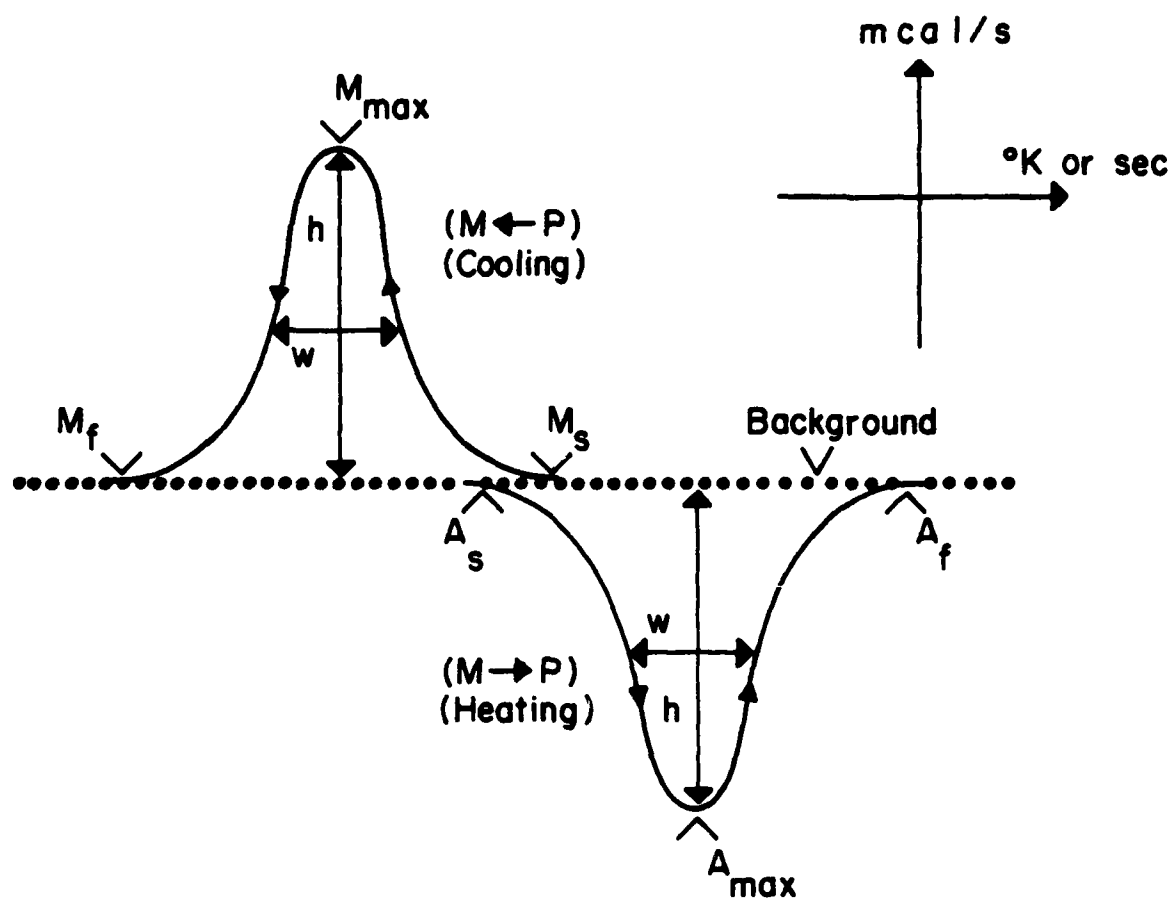


Figure 2.8 DSC Heating and Cooling Curve

### III. RESULTS AND DISCUSSION

#### A. GRAIN SIZE REFINEMENT

The refinement of the parent phase grain size of alloy B to a grain diameter of less than one tenth of a millimeter was accomplished as outlined in Experimental Procedures. This method of refinement is not only simple, but very effective in producing a small, but uniform grain size. Previous attempts to reduce the inherently large grain size in the Cu-Zn-Al family of alloys have required either the addition of a fourth element [Ref. 4], or the very careful control of time and solution treatment temperature [Ref. 5]. Although the product of each of these methods is reputed to possess identical SME and mechanical properties to the as-received alloy, each has its own drawbacks given the available alloy compositions and laboratory equipment.

During the solution treatment and subsequent quench to its martensitic phase a material of this composition must pass through first a ternary and then a binary phase region, as shown by Figure 3.1, [Ref. 3]. By traversing these regions rapidly during heating as well as cooling, any grain growth which might have occurred in them is inhibited. This leaves only the time at solution temperature for grains to seek their equilibrium diameter.

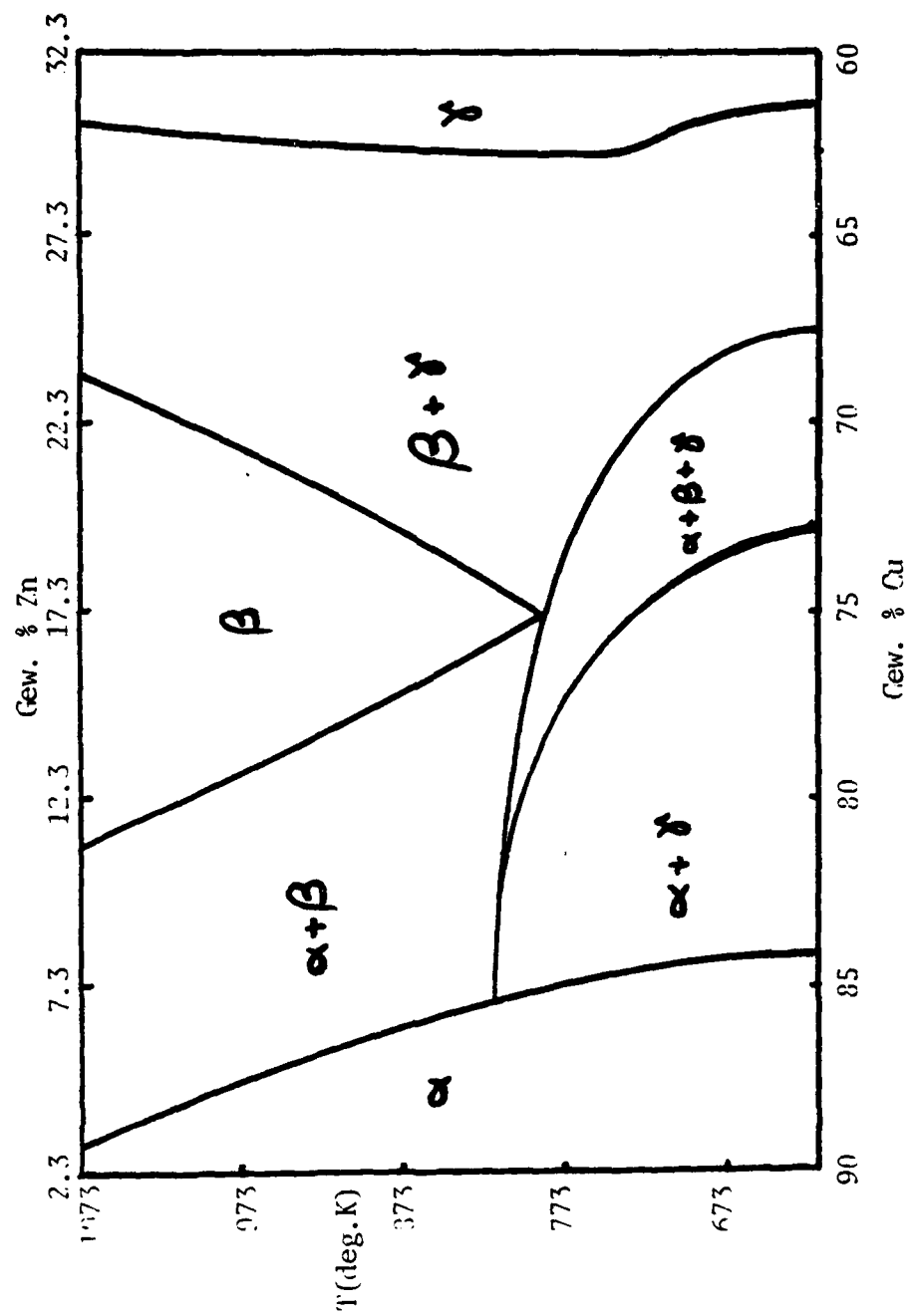


Figure 3.1 Phase Diagram of Cu-Zn-7.7w/o Al

As reported by Kelly [Ref. 6], the amount of cold work which can be introduced at room temperature is minimal. If, however, the temperature is raised to above the temperature below which stress induced martensite may be formed, ( $M_d$ ), the amount of deformation possible becomes very large; on the order of 50-100 percent. Although all possible explanations of this occurrence were not explored, the reason for this transition to ductile behavior may be hypothesized as follows.

The transition of a parent phase to martensite is rarely complete. Regardless of how rapidly a material is quenched some small amount of the stabilized parent phase will be present; usually in the prior parent phase grain boundaries. During cold work while at temperatures below  $M_d$ , the retained parent phase will be immediately transformed into stress induced martensite. In addition, Delaey, et. al., [Ref. 7], have shown that thermal martensite created by quenching into a medium which is below  $M_s$  causes the formation of stress induced martensite plates which intersect the thermal martensite plates between variants. The presence and formation at grain boundaries of stress induced martensite may serve as an inhibitor of dislocation movement and, therefore, prevent large scale deformation. The elimination of this inhibition by heating above  $M_d$  allows a large degree of deformation to occur and, consequently, a marked increase in dislocation density.

The increase of dislocation density through warm working, coupled with the short time at solution temperature, provides a simple and repeatable method of producing a fine grained specimen.

#### B. CYCLIC EFFECTS ON MARTENSITE START TEMPERATURE

The data produced by this study is consistent with the idea that multiple thermal cycling establishes preferred nucleation sites for the martensitic transformation and stabilizes the martensite. As previously reported by Perkins and Muesing [Ref. 8], as these preferred sites are "learned," martensite nucleates and grows more readily and  $M_s$  increases steadily. This effect is illustrated by Figures 3.2 through 3.8.

Significant work by Pops and Massalski [Ref. 9], in 1964 showed that martensite formation in Cu-Zn alloys takes place in two stages. Upon cooling the initial "thermoelastic" martensite nucleates and grows relatively slowly. As cooling continues, the second stage appears as "burst" martensite which grows at the speed of sound and, the formation of which, diminishes and then disappears with thermal cycling. Pops and Massalski [Ref. 9], also showed that the formation of burst martensite produces lattice defects and some degree of plastic deformation in the parent lattice.

Evidence from work done by Perkins and Muesing [Ref. 8], along with that done by Kajiwara and Kikuchi [Ref. 10],



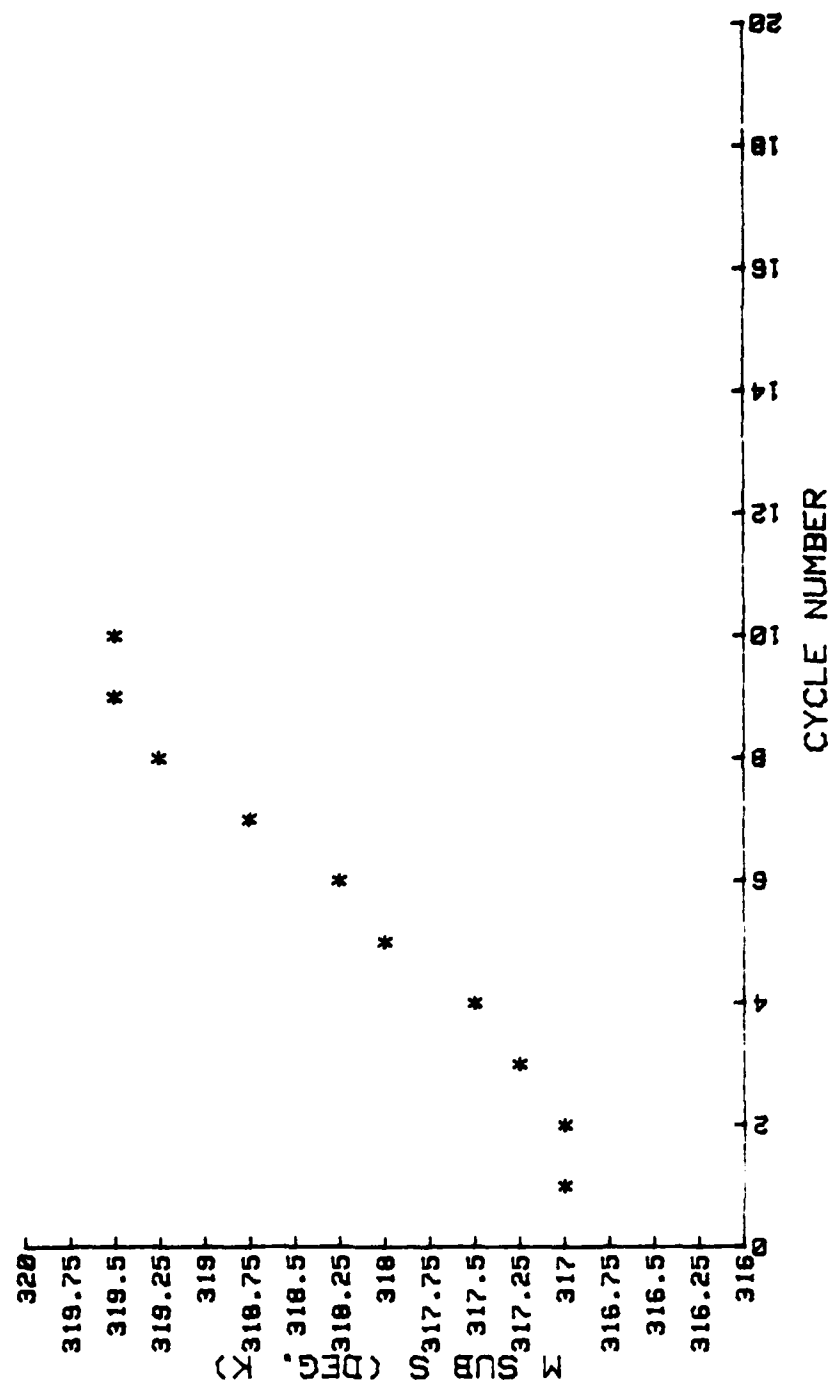


Figure 3.2 Ms vs. Cycle No. for a Grain Size of 0.08mm.

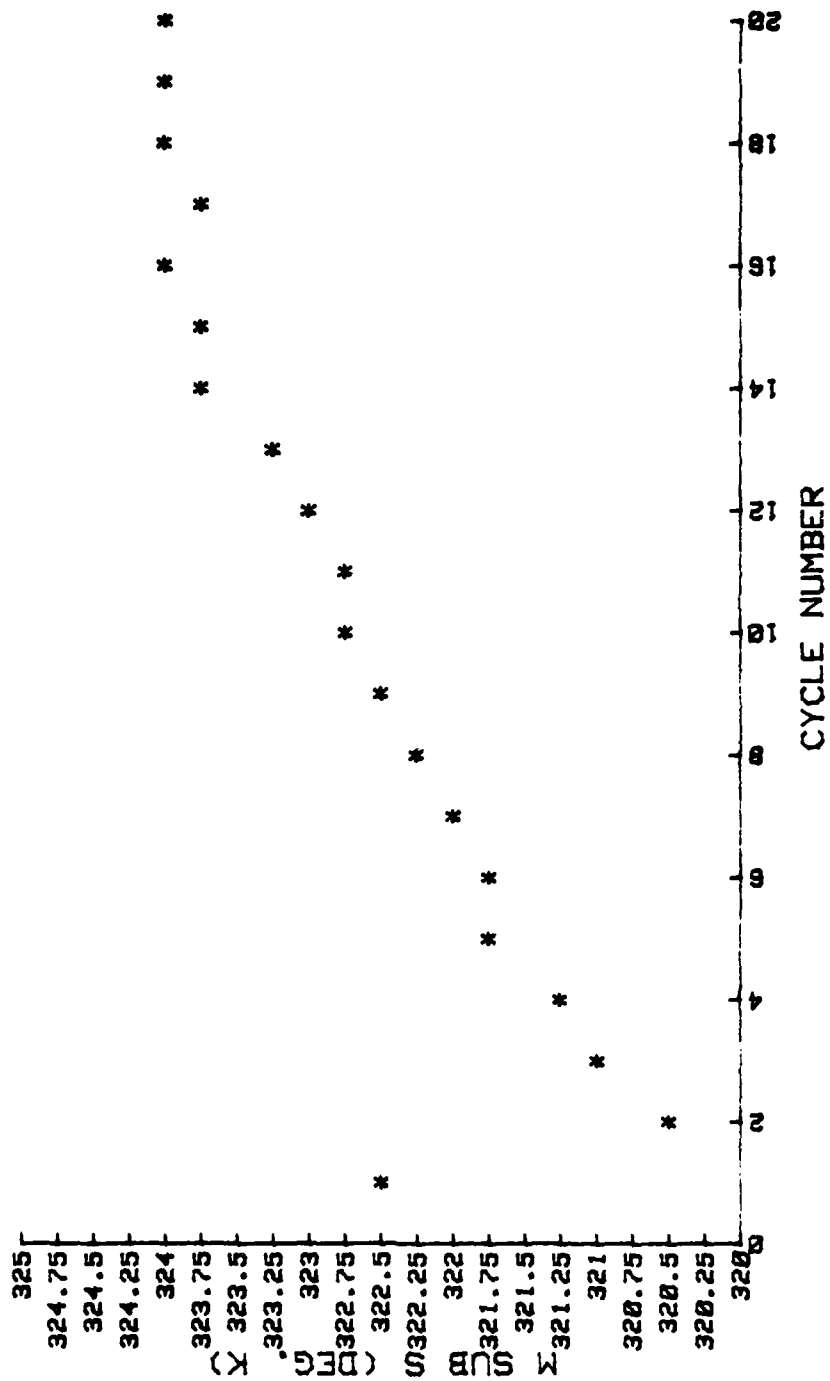


Figure 3.3 Ms vs. Cycle No. for a Grain Size of 0.21mm.

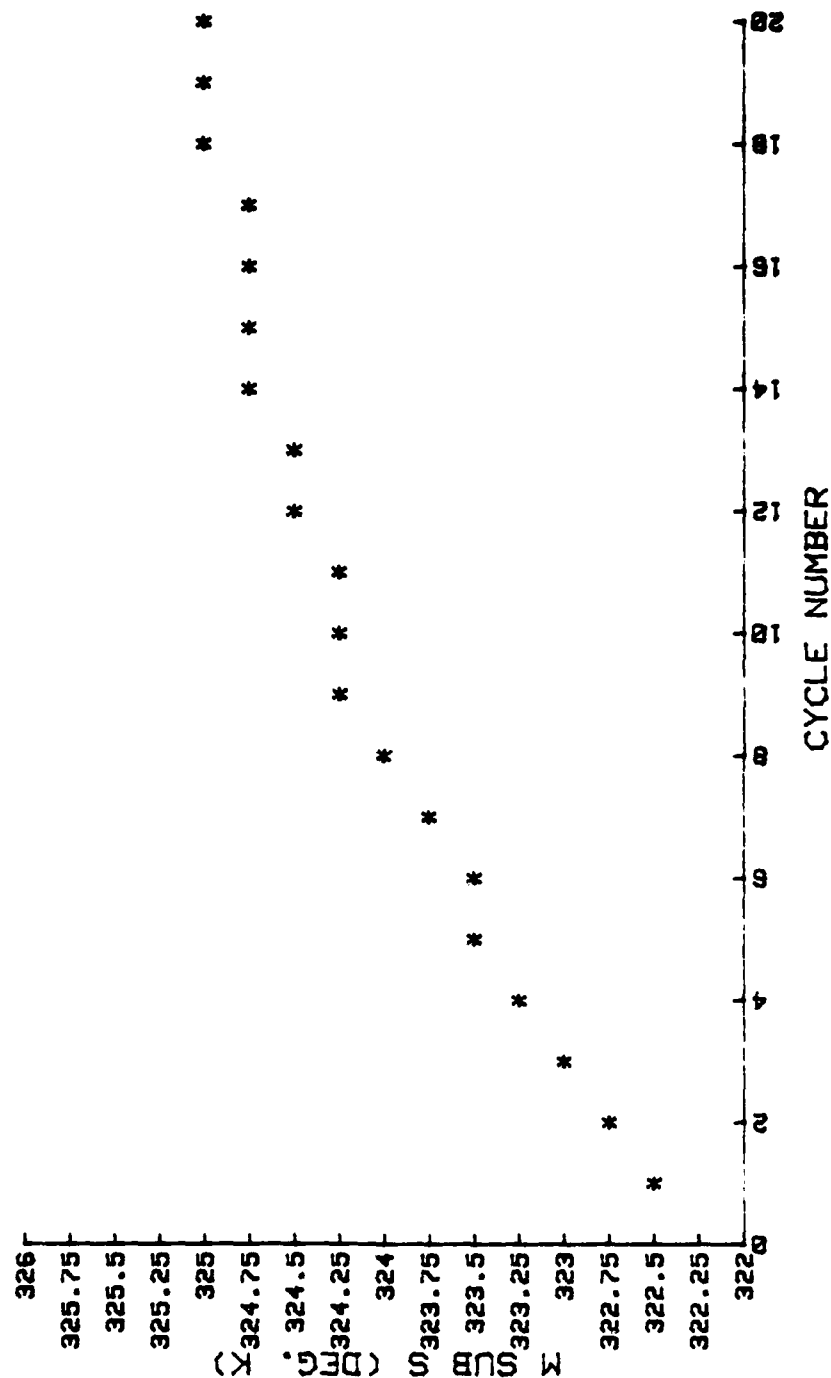


Figure 3.4 Ms vs. Cycle No. for a Grain Size of 0.38mm.

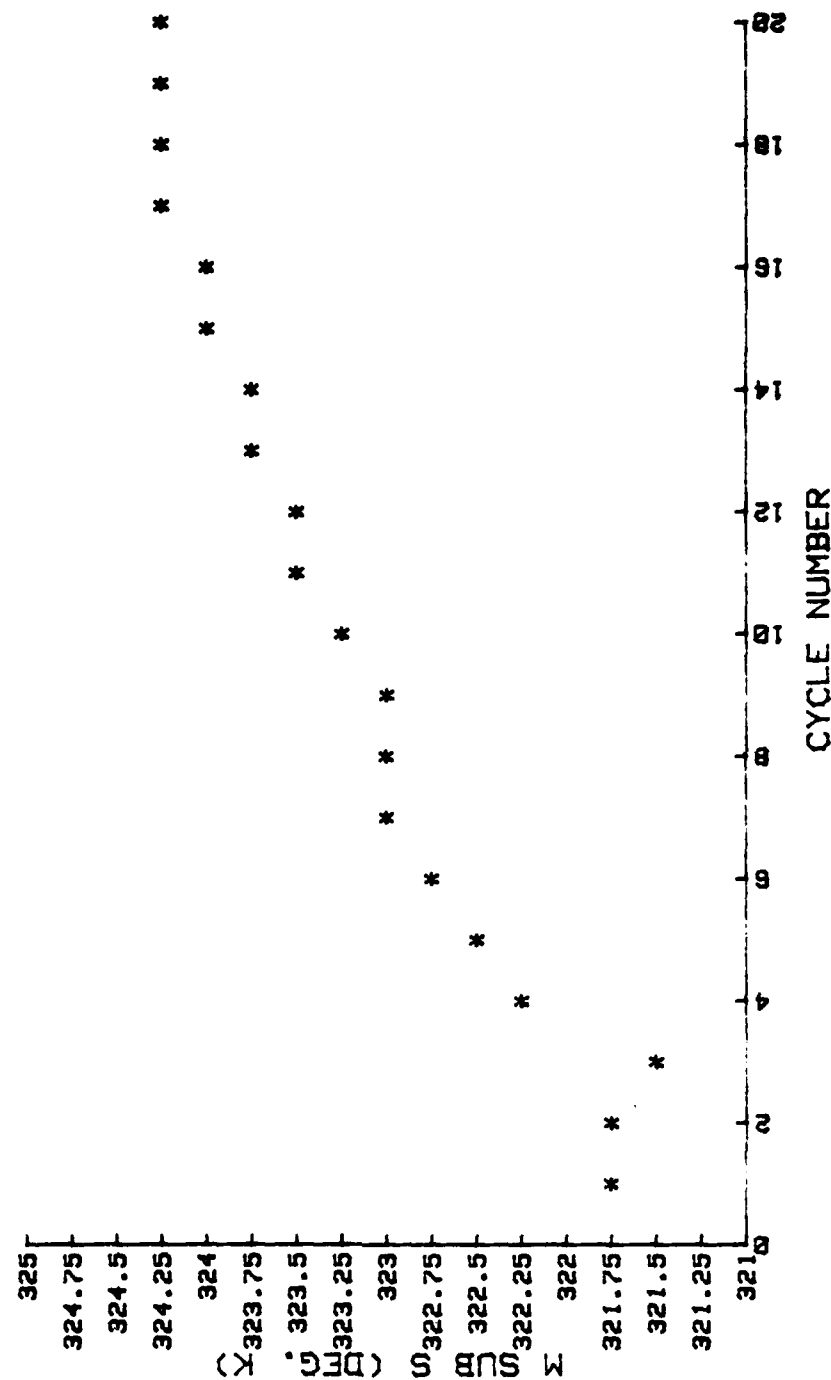


Figure 3.5 Ms vs. Cycle No. for a Grain Size of 0.53mm.

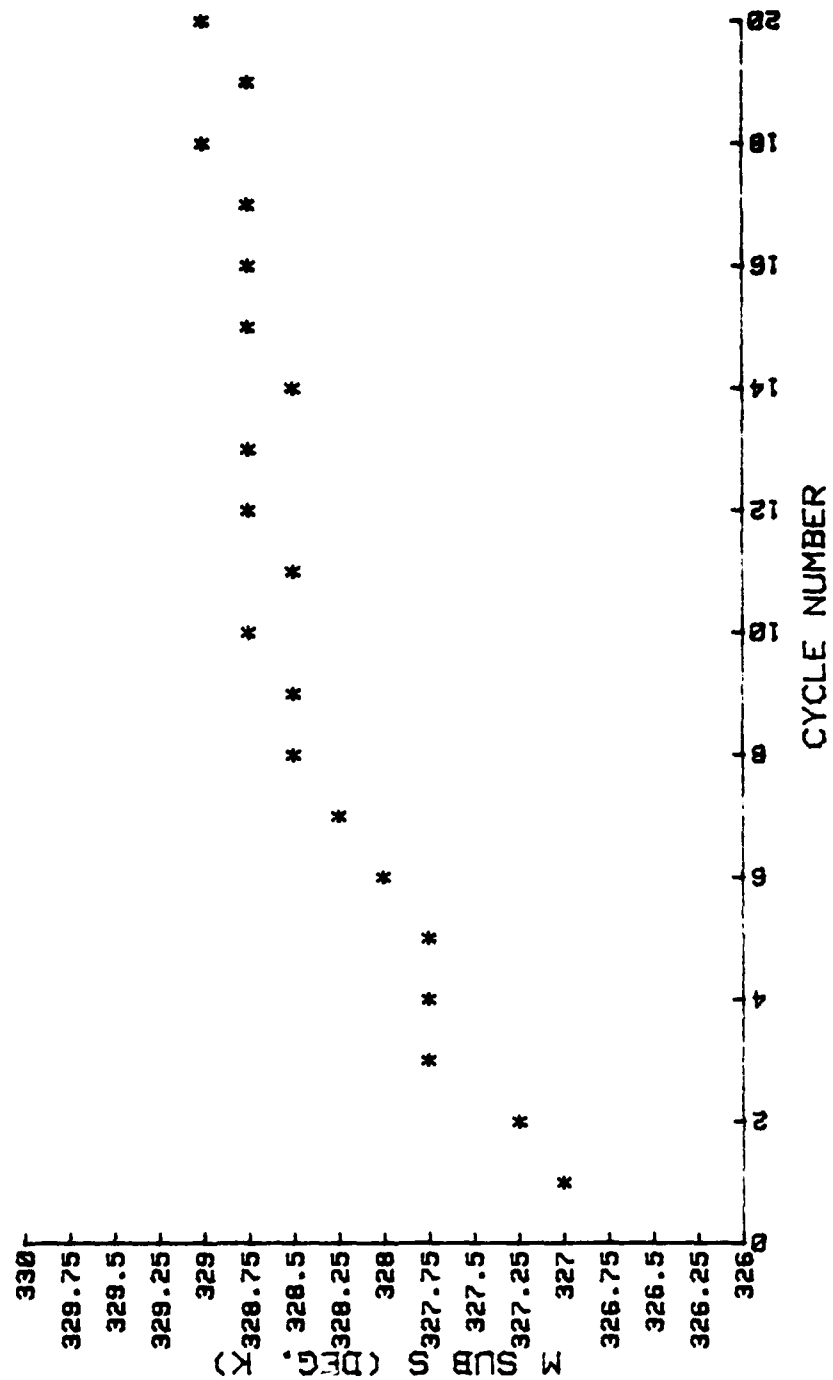


Figure 3.6 Ms vs. Cycle No. for a Grain Size of 0.63mm.

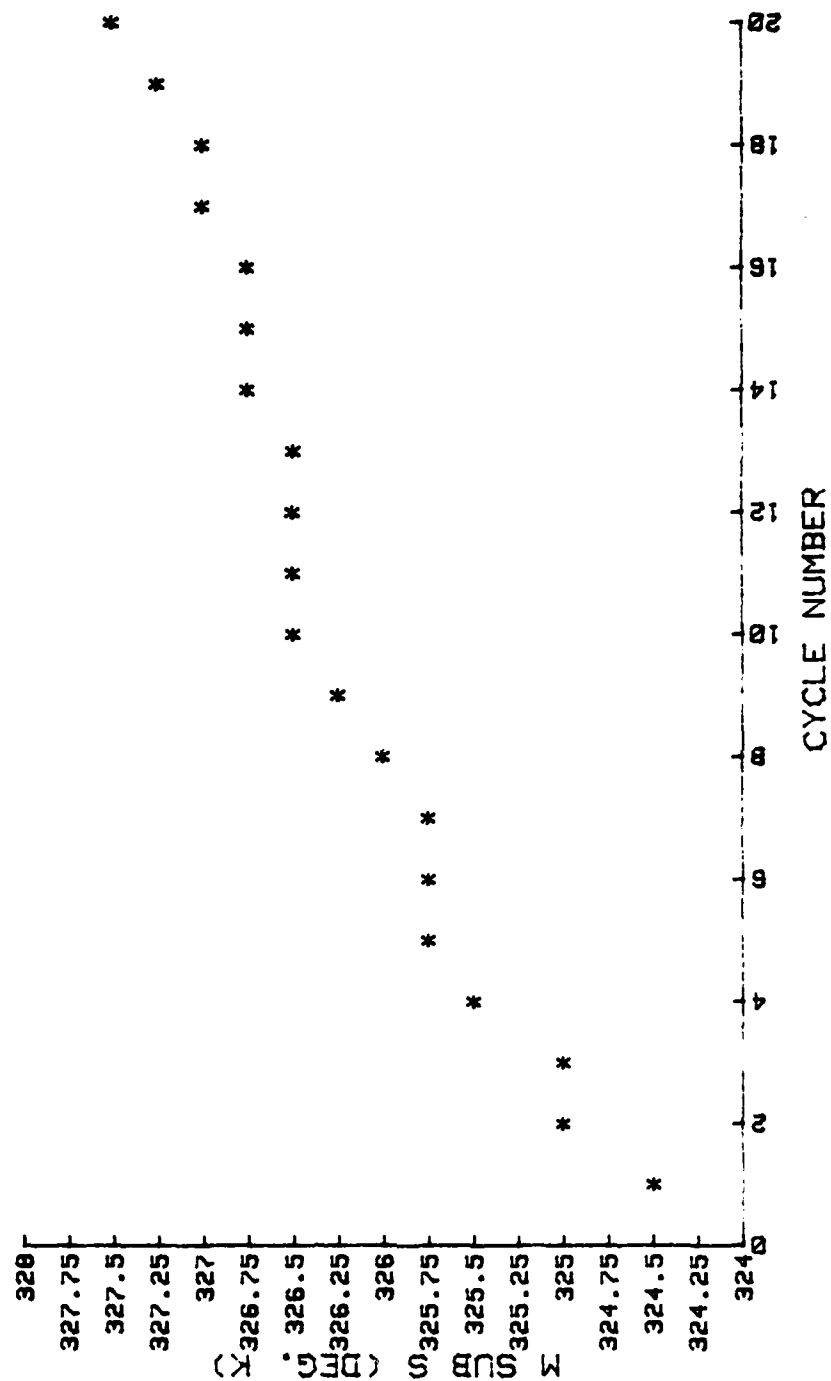


Figure 3.7 Ms vs. Cycle No. for a Grain Size of 0.82mm.

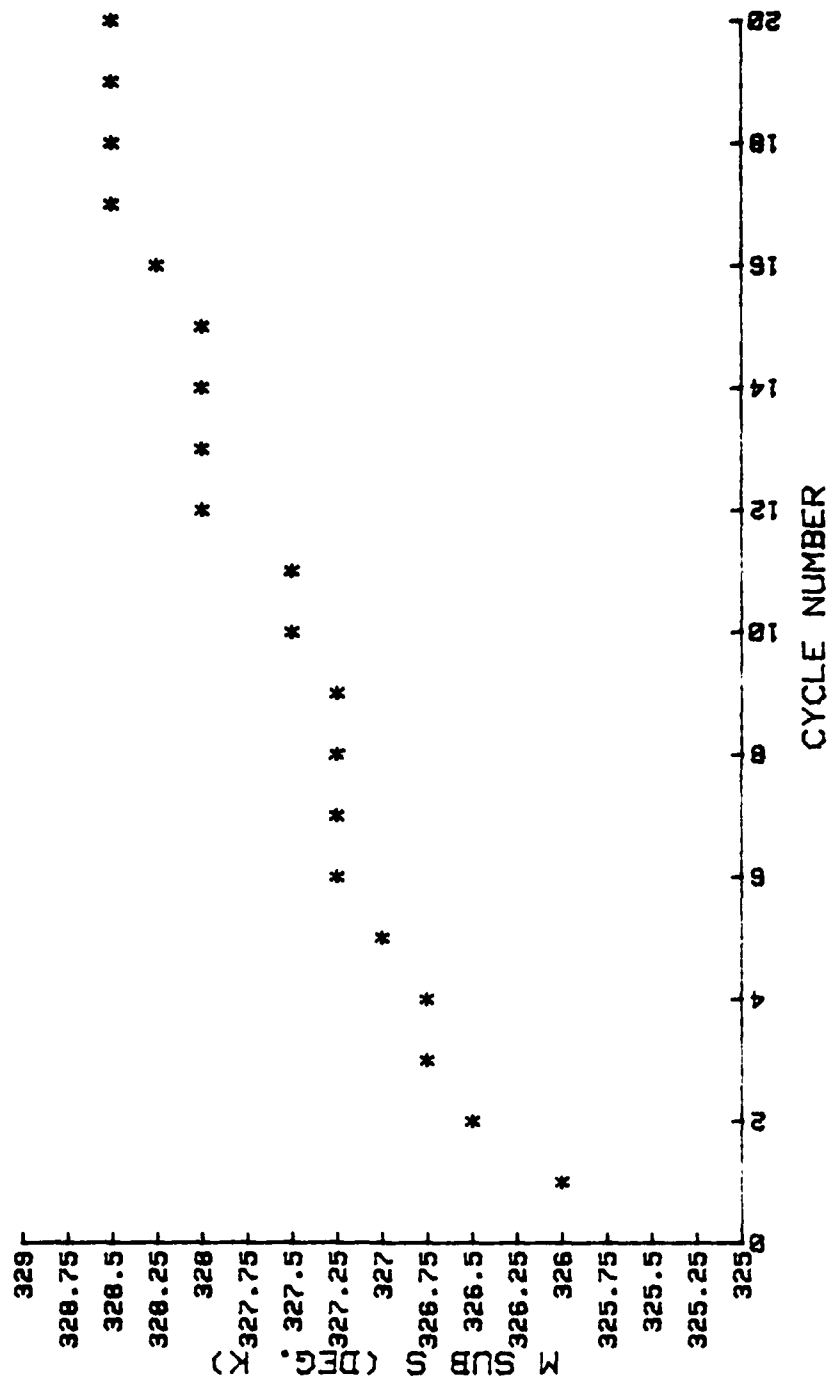


Figure 3.8 Ms vs. Cycle No. for a Grain Size of 1.01mm.

both on TEM observations of thermally cycled Cu-Zn alloys, mutually corroborate the existence of a dislocation substructure in multiple-cycled samples which serves to stabilize the martensite, thereby raising the  $M_s$ .

### C. GRAIN SIZE EFFECT ON $M_s$ STABILIZATION

A more subtle effect than the increase of  $M_s$  over multiple cycles is the rate at which this stabilization takes place in specimens of different parent phase grain sizes. Although the martensite phase has no distinct grain structure, the beta grain boundaries still appear as lines of interruption of plate growth, giving the martensite a pseudo-grain structure. The number of cycles required for a one and one-half degree increase in  $M_s$  increases with increasing grain size. That is to say, that the rate of stabilization is inversely proportional to specimen grain size. This rate, found by dividing one and one-half degrees by the required number of cycles, is plotted against grain size in Figure 3.9. Further illustration of this effect is seen in the change of the shape of the curves in Figures 3.10 to 3.29.

This result is predictable by analyzing the mechanism by which stabilization of  $M_s$  occurs. Again, as martensite nucleation sites are learned, less energy is required for the nucleation process to occur. Underlying this phenomenon is the building up of the substructure of dislocations. In a large grained specimen the generation of this substructure



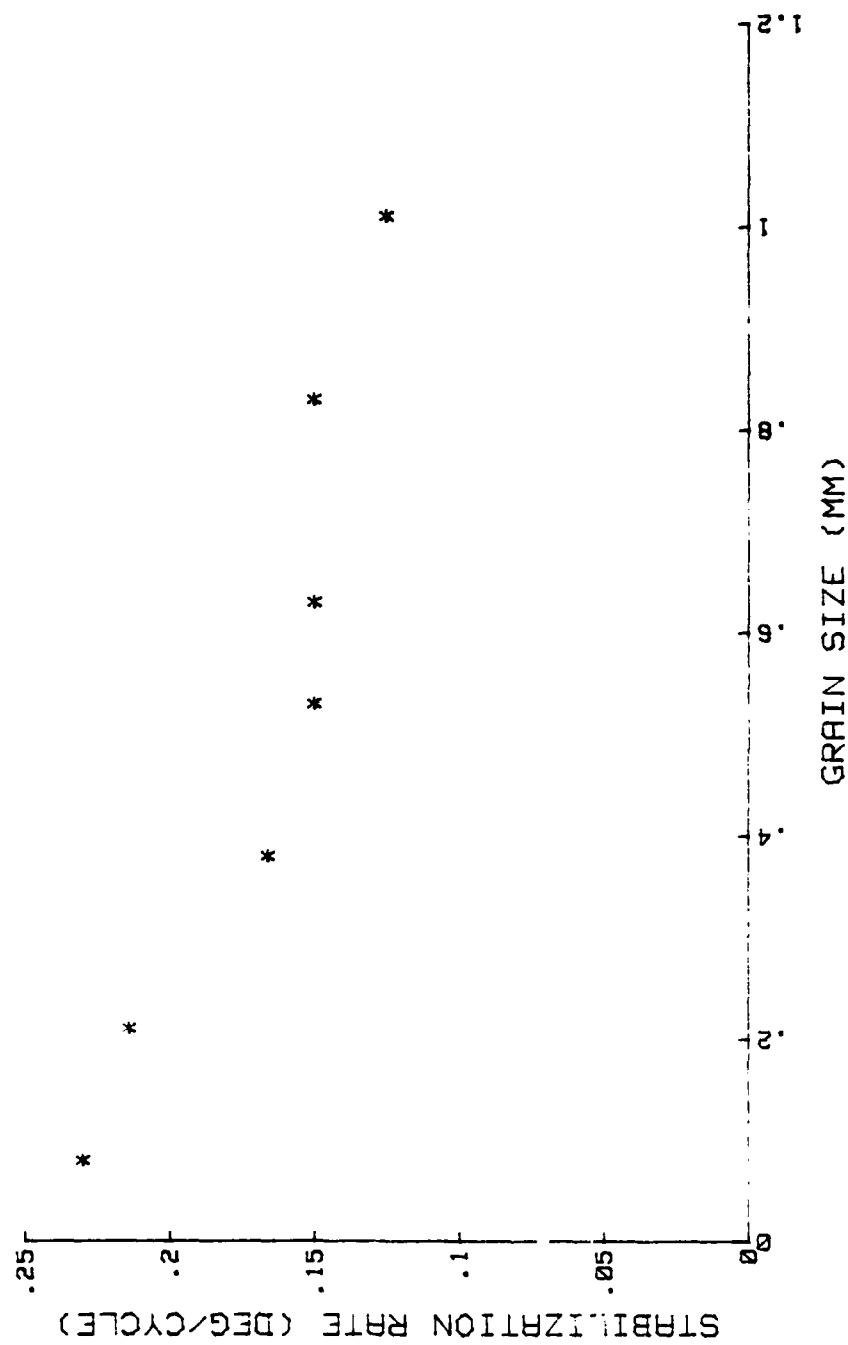


Figure 3.9 Stabilization Rate vs. Grain Size.

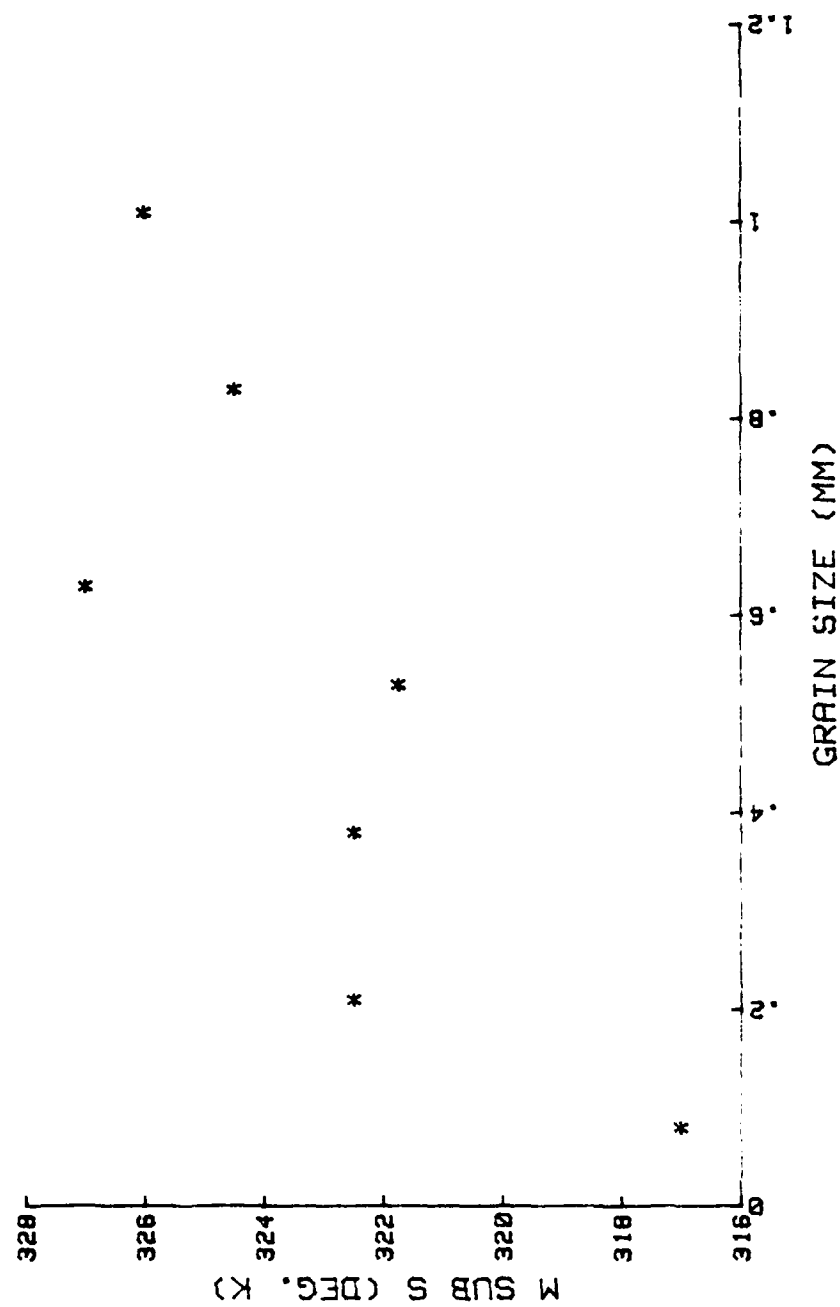


Figure 3.10 Ms vs. Grain Size for Cycle 1.

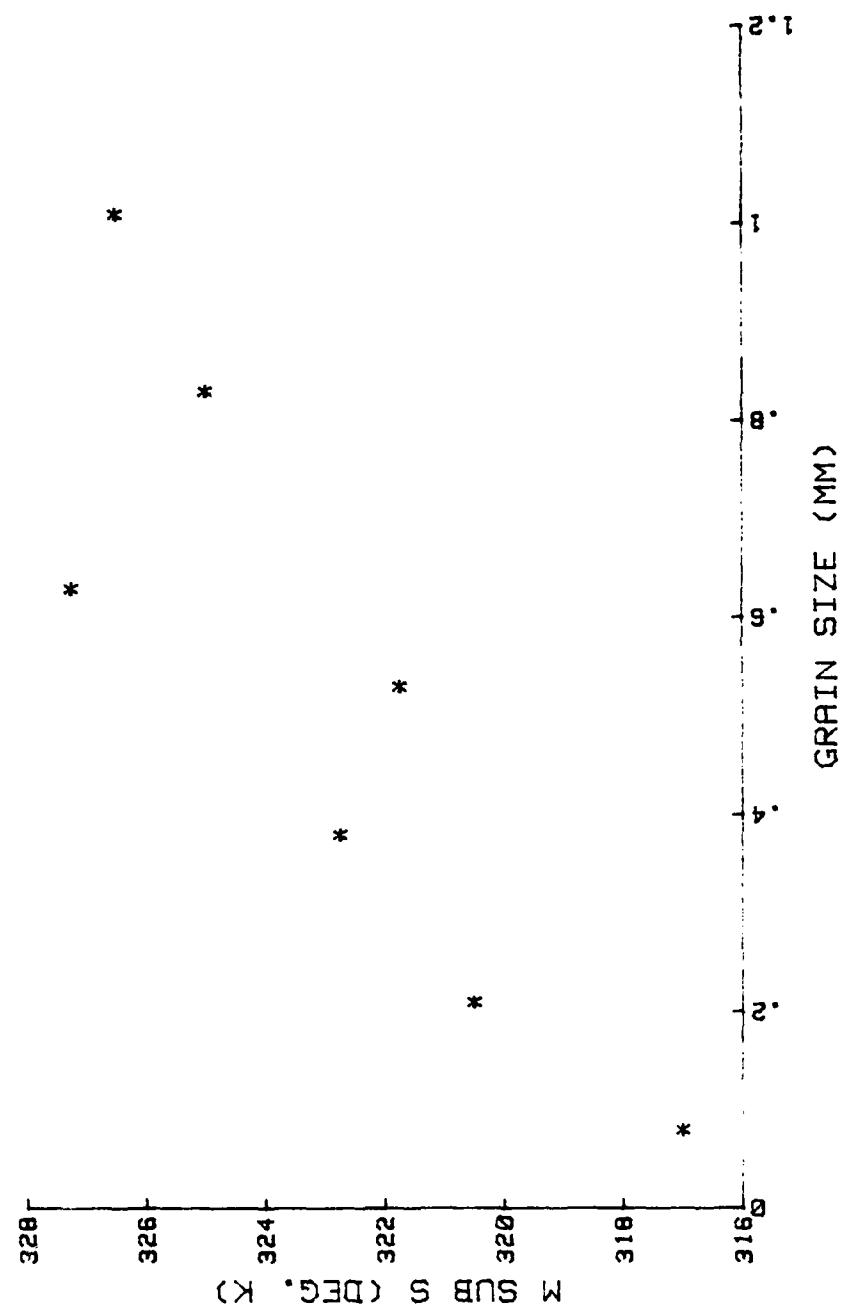


Figure 3.11 Ms vs. Grain Size for Cycle 2.

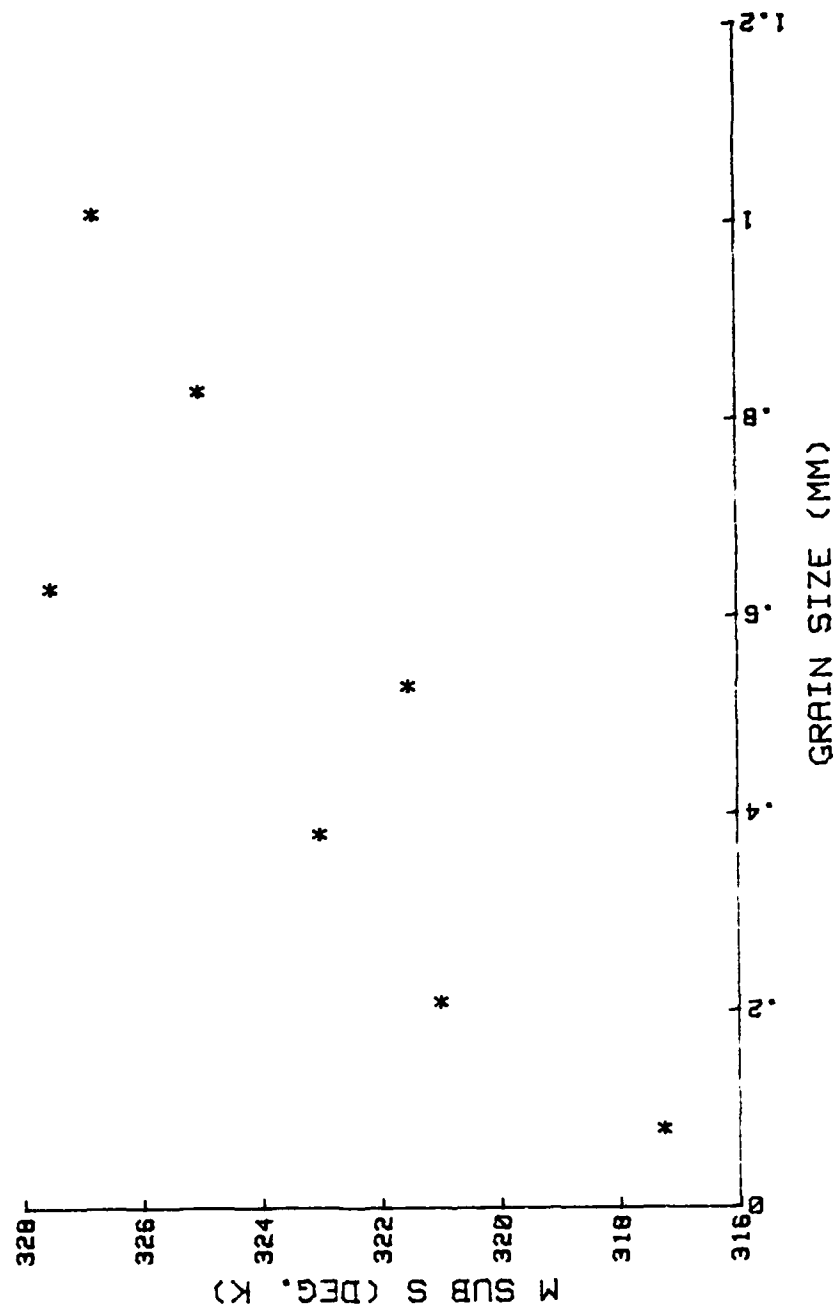


Figure 3.12 Ms vs. Grain Size for Cycle 3.

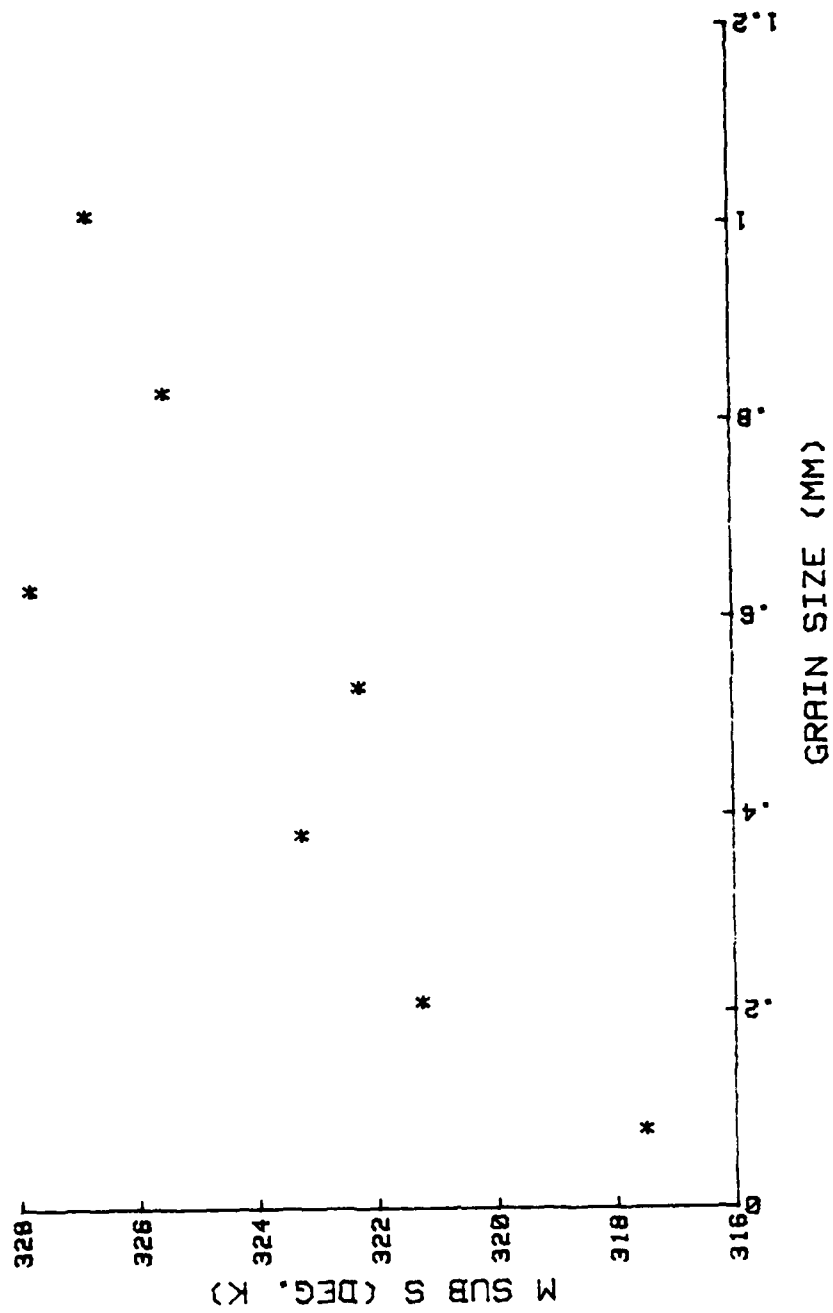


Figure 3.13 Ms vs. Grain Size for Cycle 4.

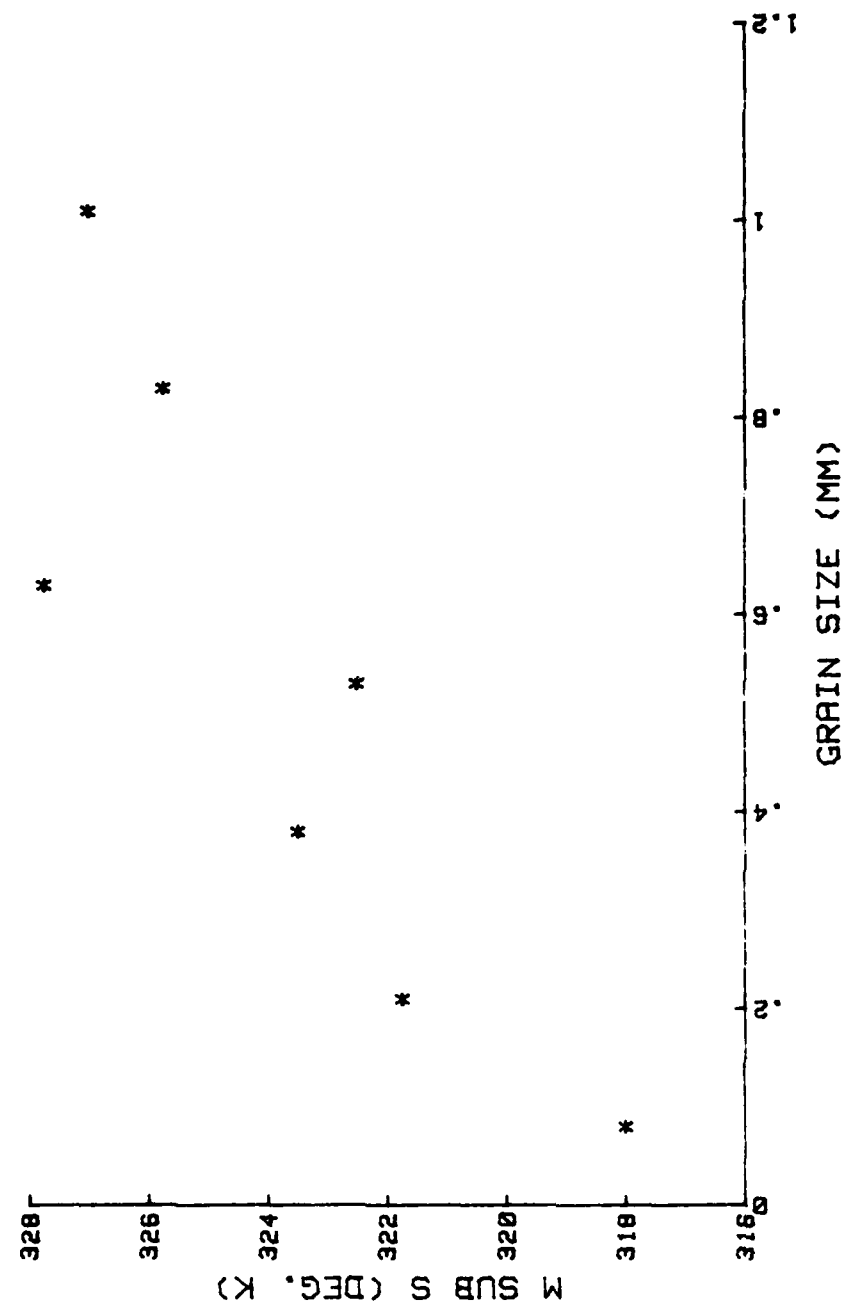


Figure 3.14  $M_s$  vs. Grain Size for Cycle 5.

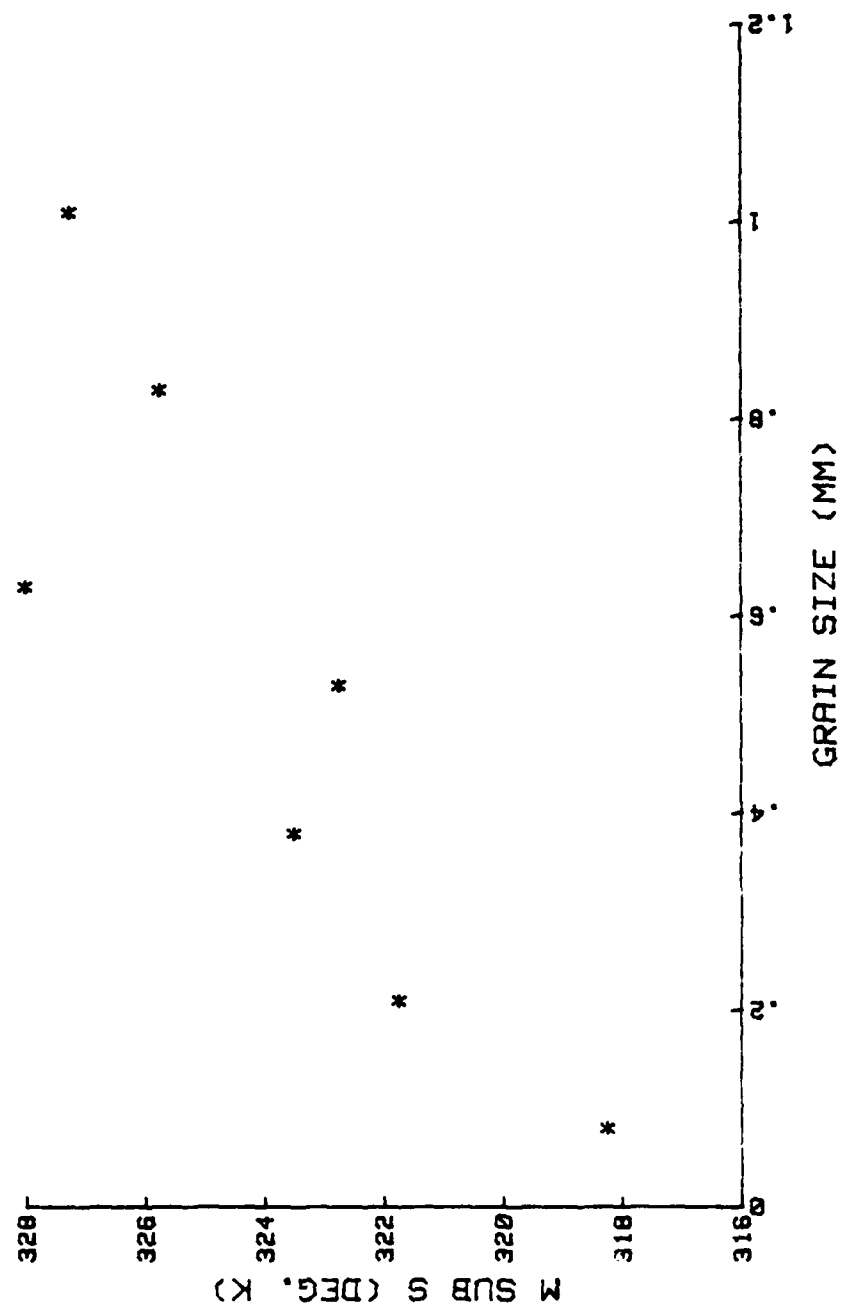


Figure 3.15 Ms vs. Grain Size for Cycle 6.

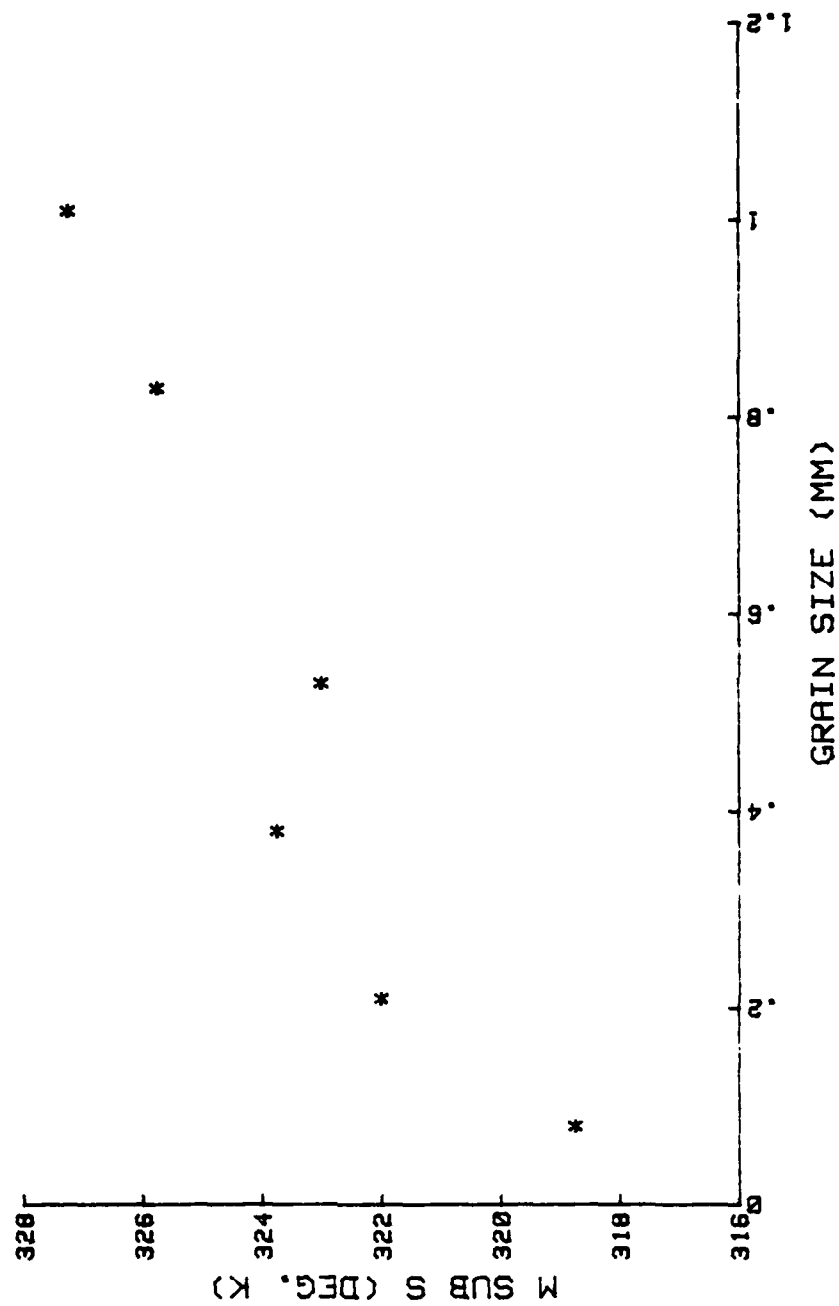


Figure 3.16 Ms vs. Grain Size for Cycle 7.



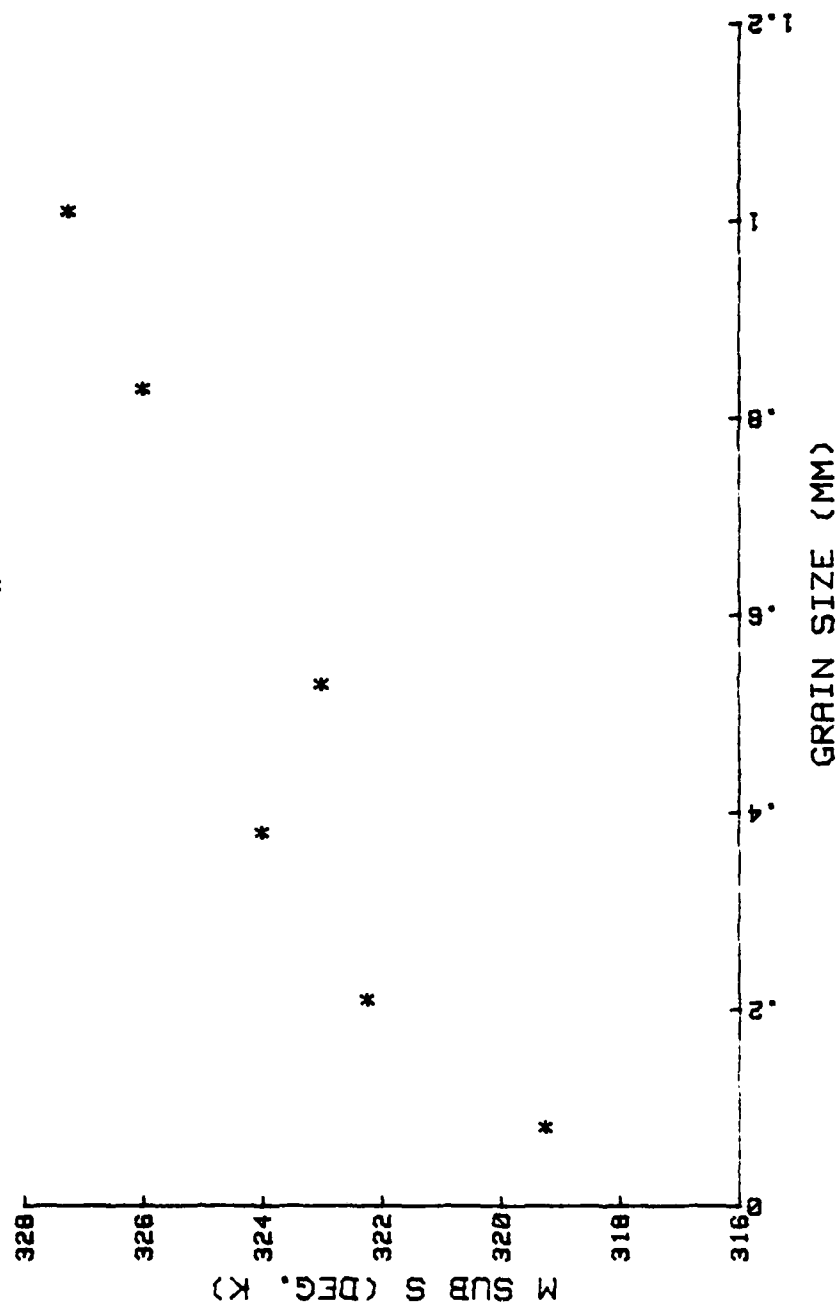


Figure 3.17 Ms vs. Grain Size for Cycle 8.

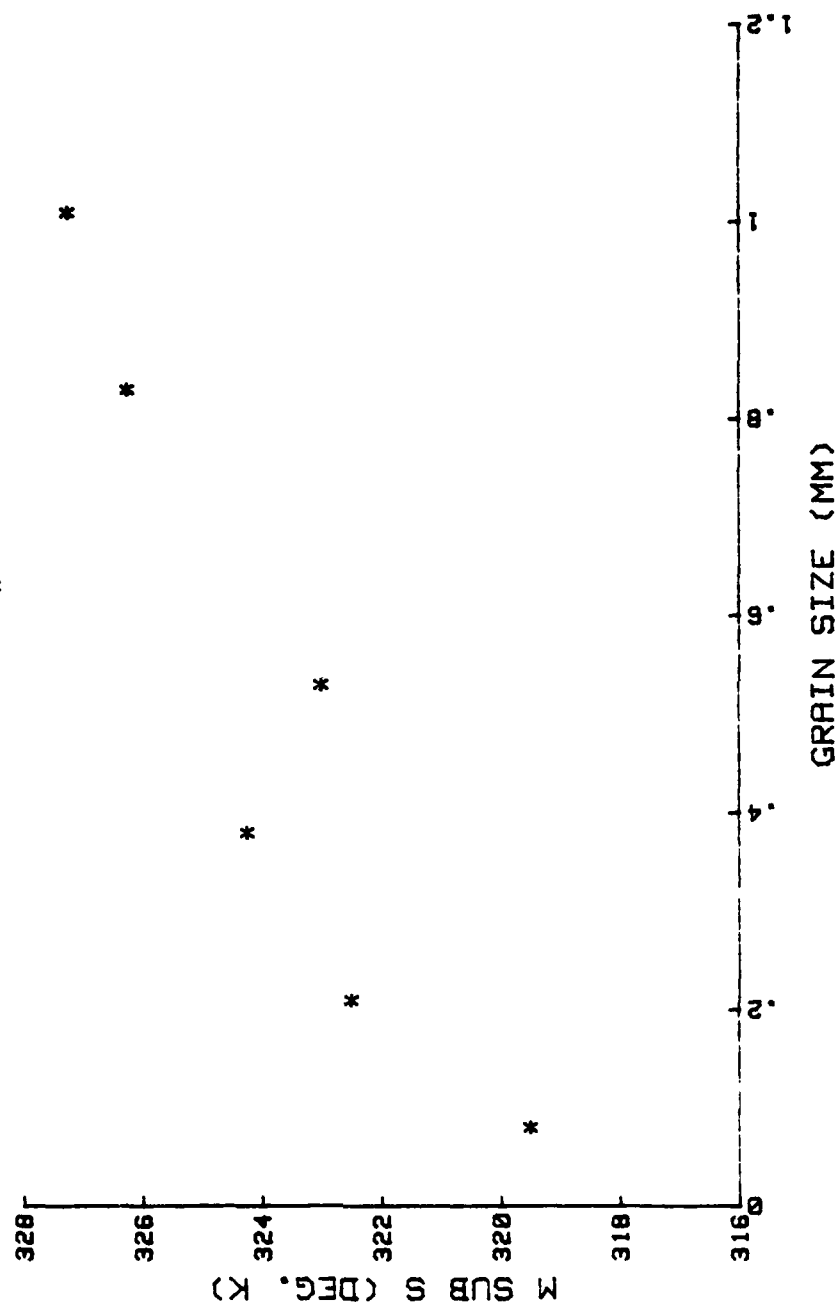


Figure 3.18 Ms vs. Grain Size for Cycle 9.

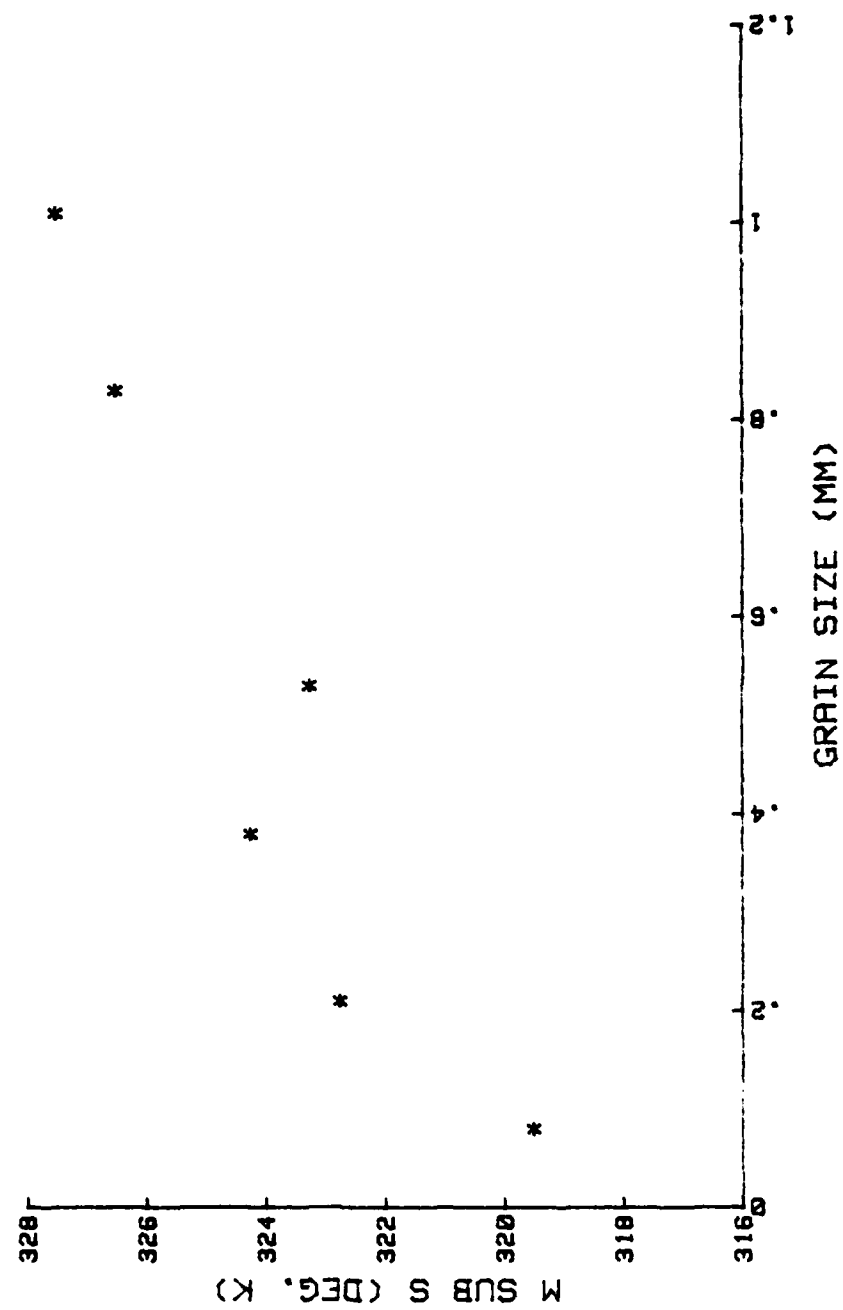


Figure 3.19 Ms vs. Grain Size for Cycle 10.

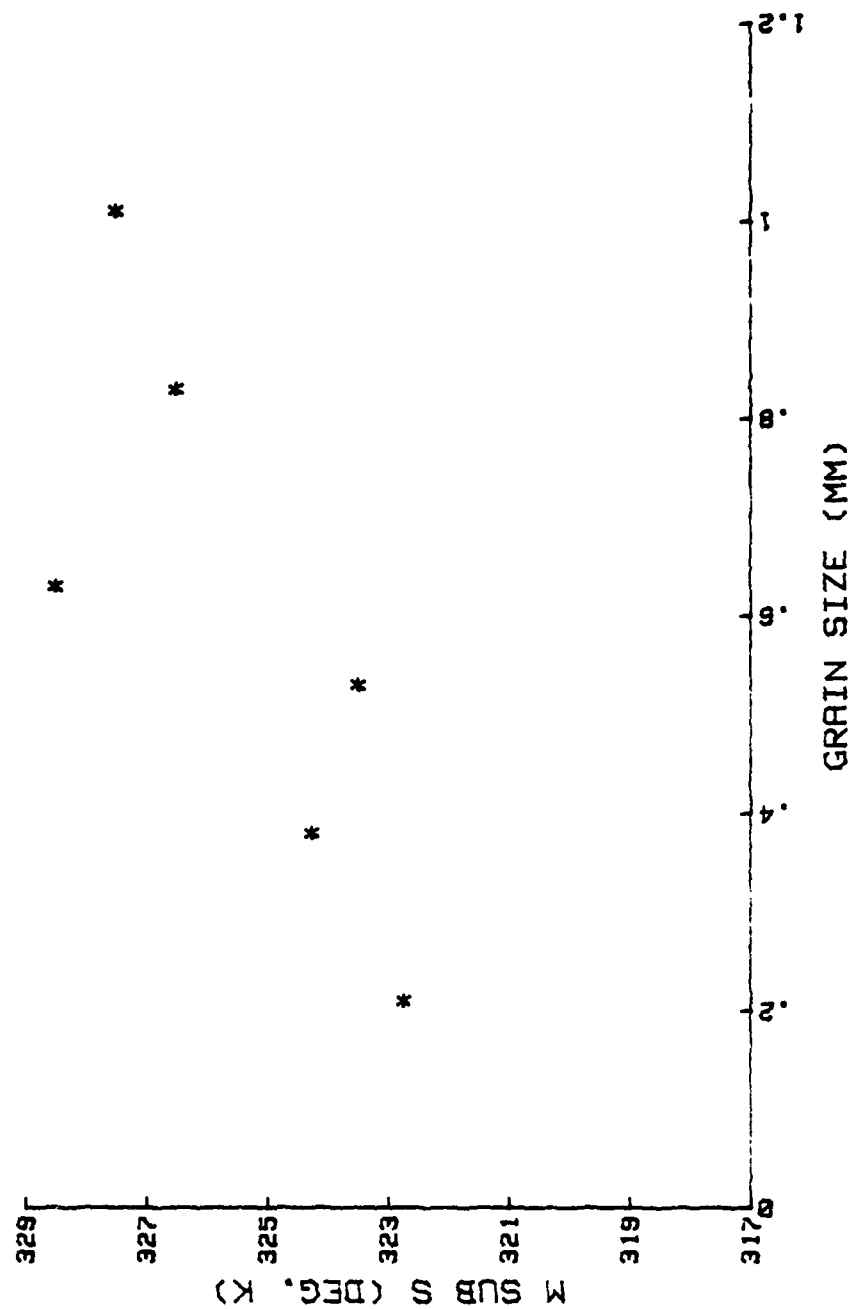


Figure 3.20 Ms vs. Grain Size for Cycle 11.

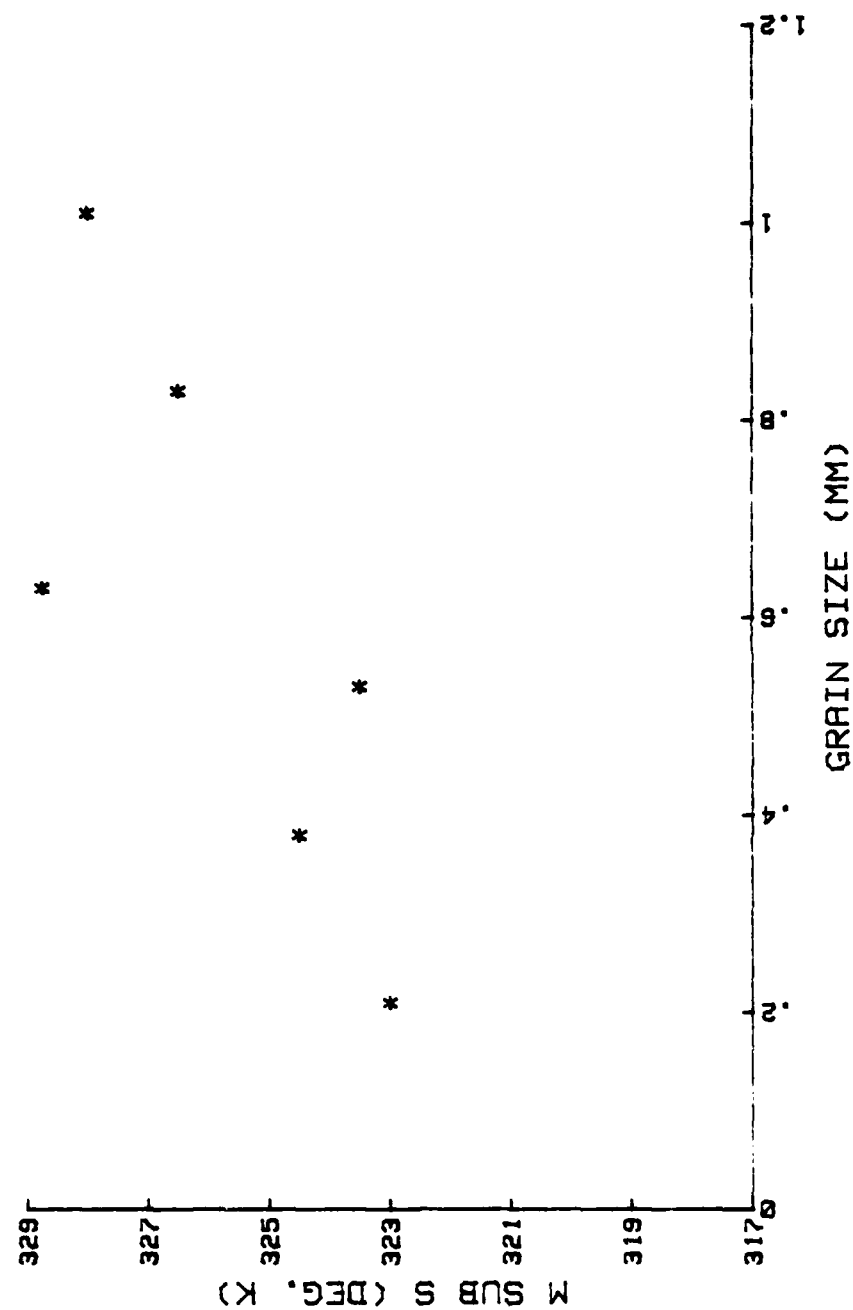


Figure 3.21  $M_s$  vs. Grain Size for Cycle 12.

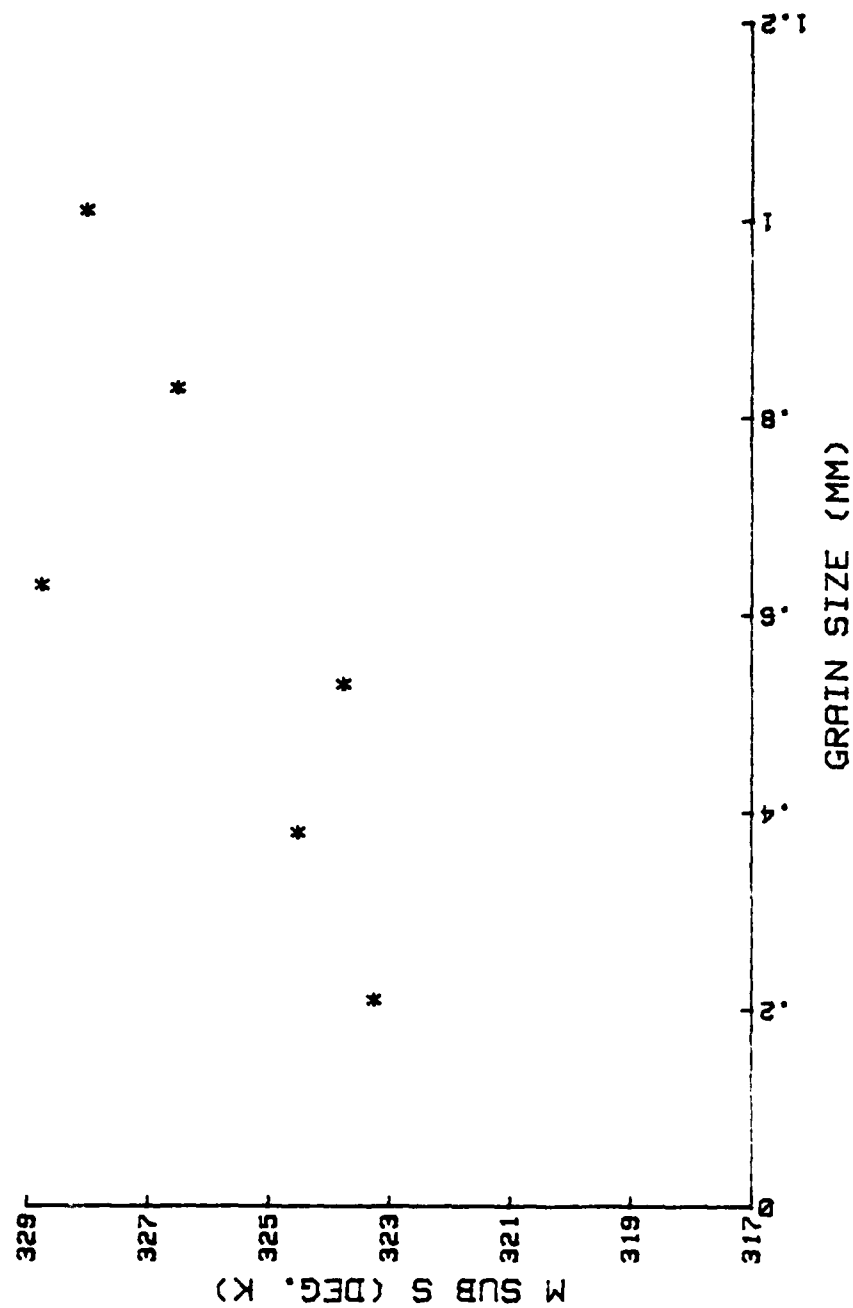


Figure 3.22 Ms vs. Grain Size for Cycle 13.

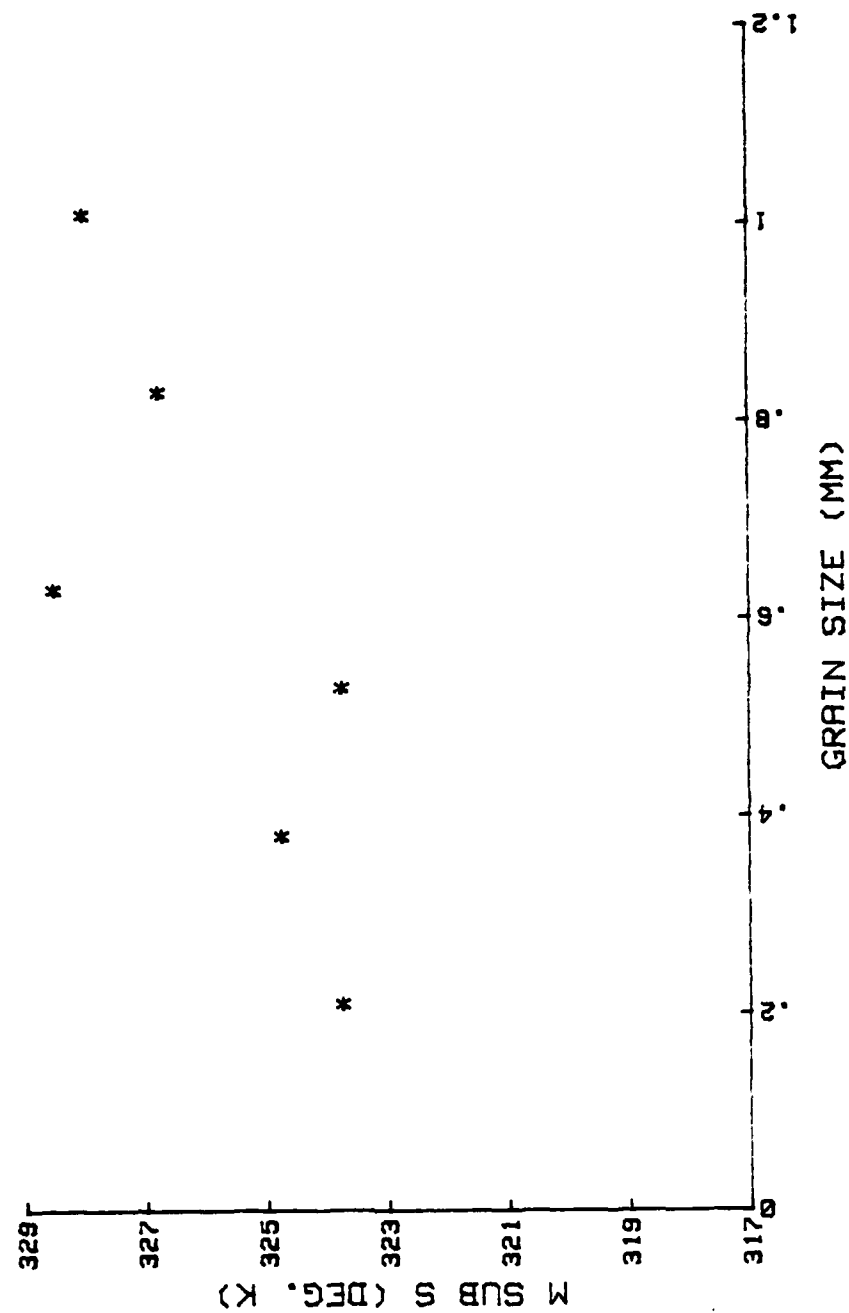


Figure 3.23 Ms vs. Grain Size for Cycle 14.

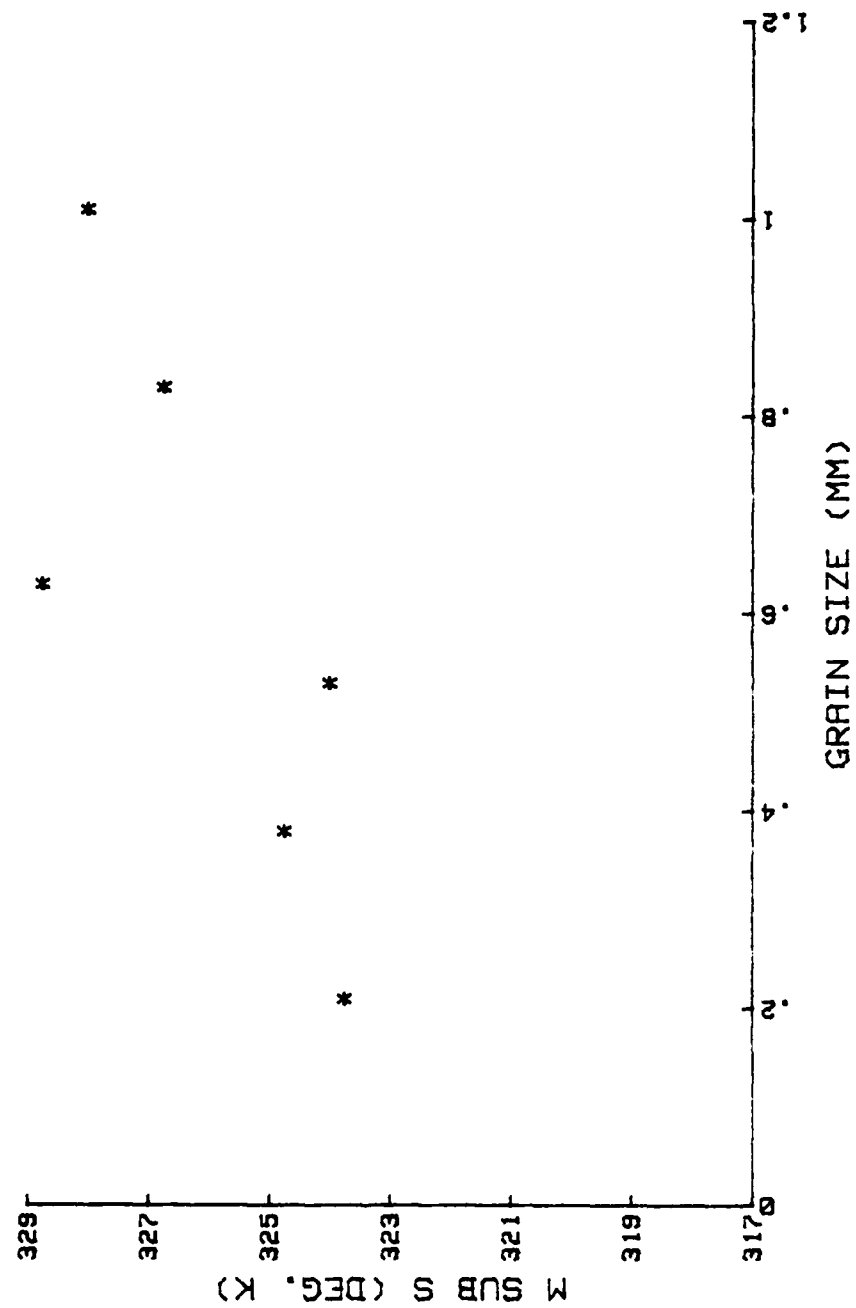


Figure 3.24 Ms vs. Grain Size for Cycle 15.



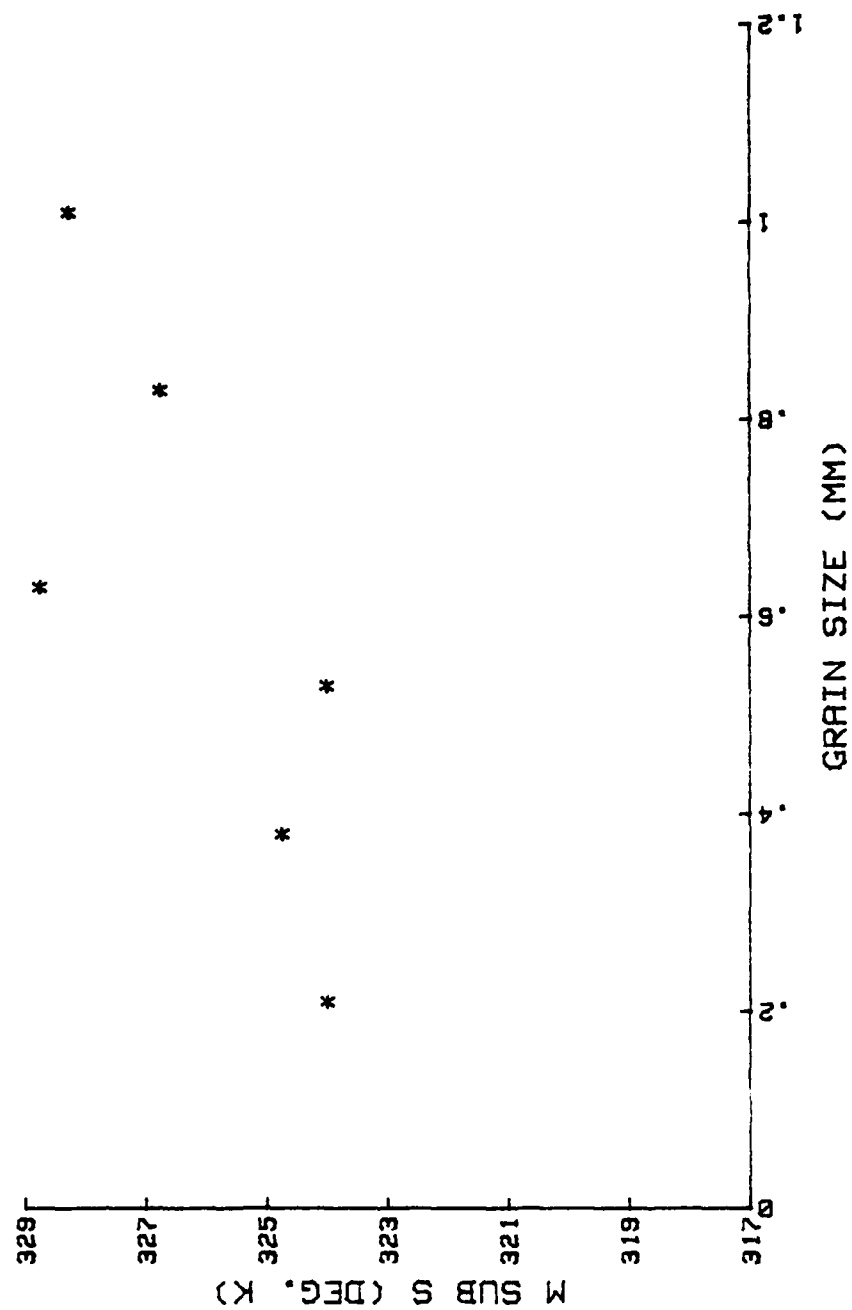


Figure 3.25 Ms vs. Grain Size for Cycle 16.

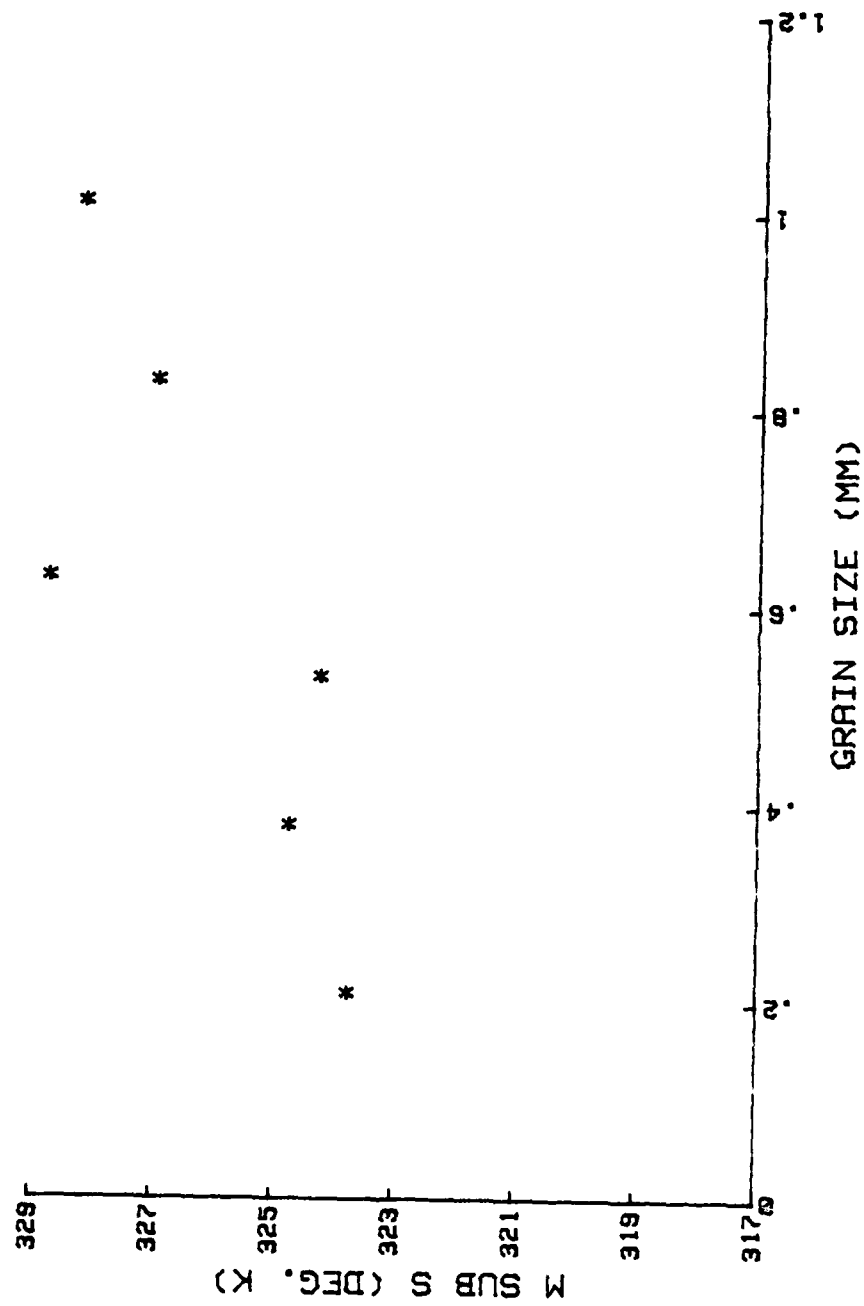


Figure 3.26 Ms vs. Grain Size for Cycle 17.

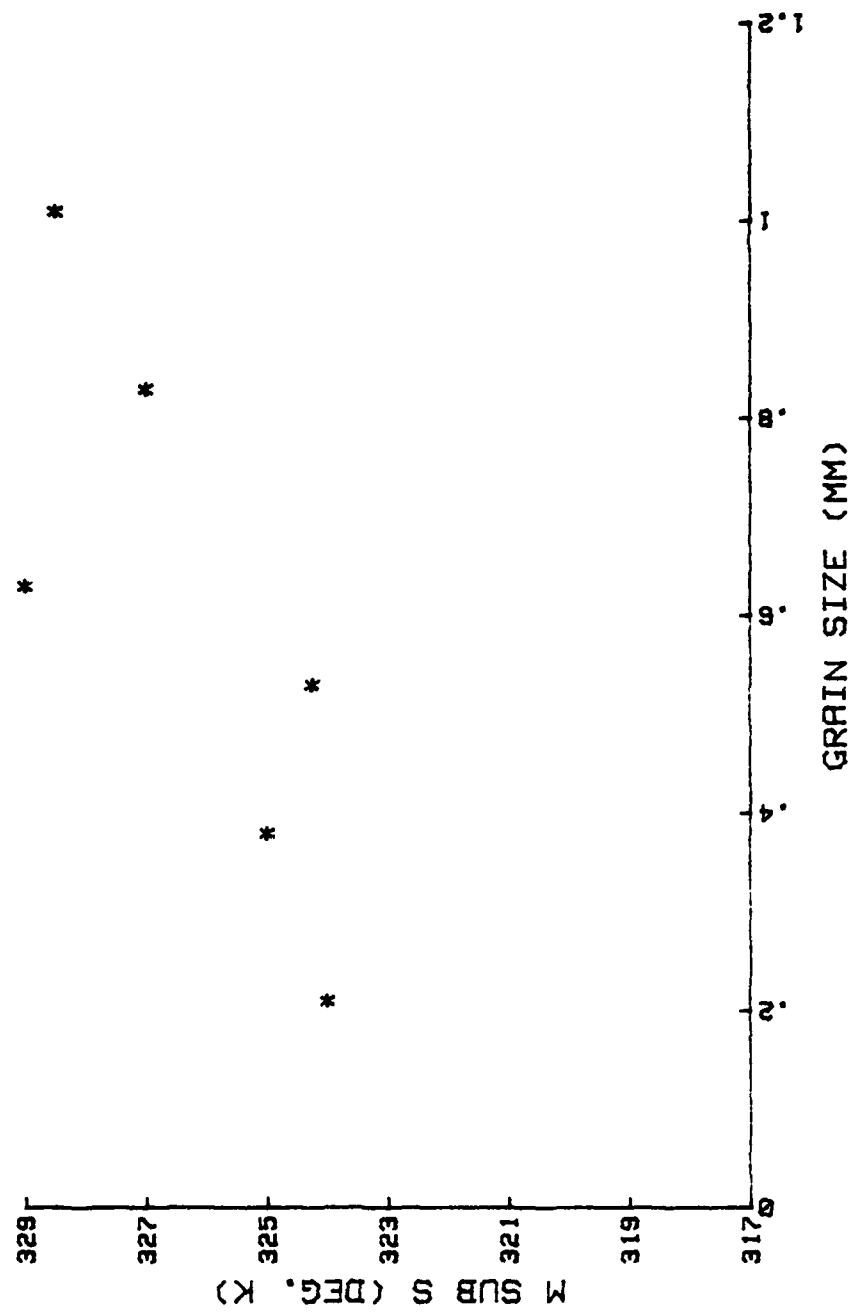


Figure 3.27  $M_s$  vs. Grain Size for Cycle 18.

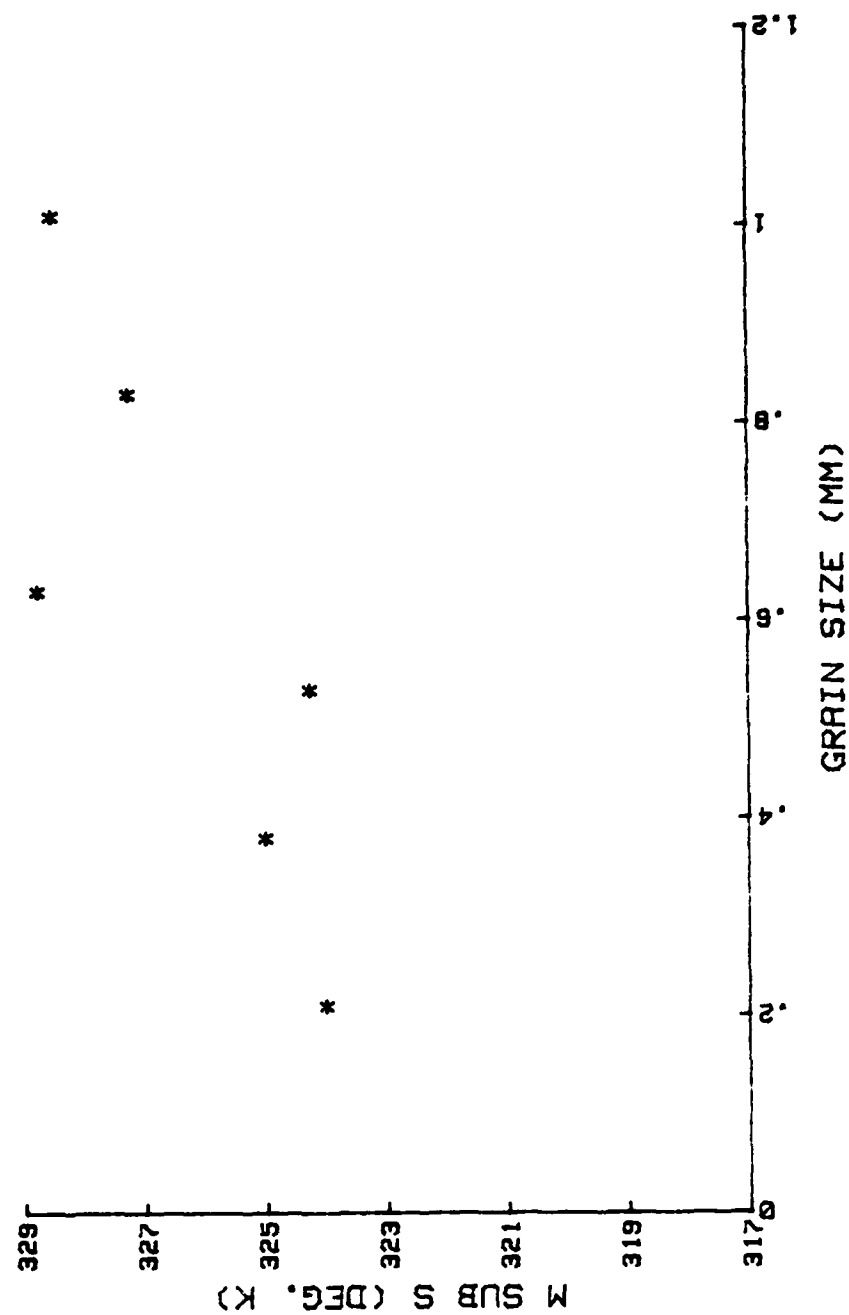


Figure 3.28 Ms vs. Grain Size for Cycle 19.

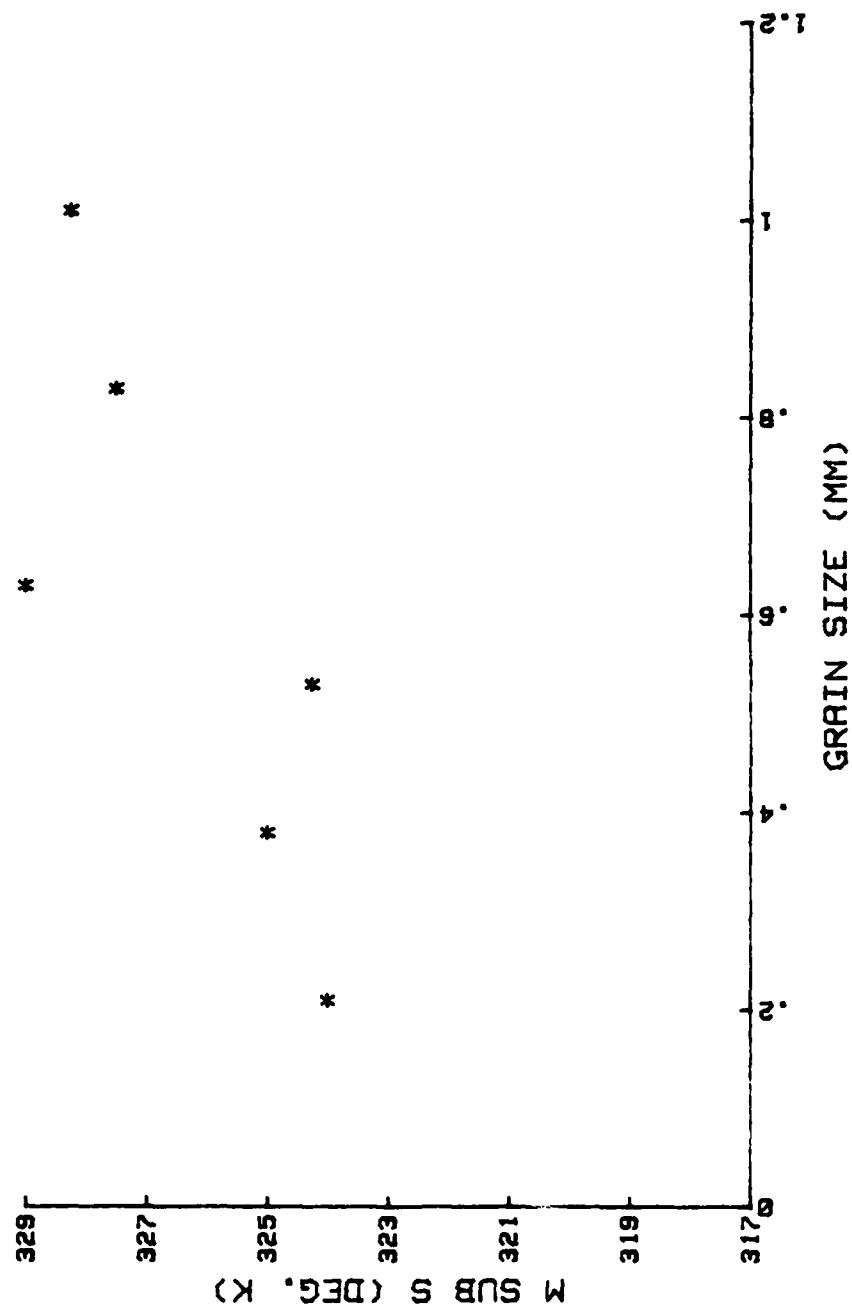


Figure 3.29 Ms vs. Grain Size for Cycle 20.

is carried out without the interference of a large number of grain boundaries, whose effect is to annihilate individual dislocations. The dislocation substructure is readily formed and stabilization of  $M_s$  occurs early on; hence, the large number of cycles required to obtain a given increase in  $M_s$ . In a fine grained specimen there are many grain boundaries to act as dislocation annihilators and the dislocation substructure has difficulty in establishing a foothold. As cycling progresses, each small addition to the dislocation substructure causes a marked decrease in the energy required for transformation; hence, the small number of cycles required to obtain a given rise in  $M_s$ .

#### D. INITIAL MARTENSITE STABILIZATION DUE TO QUENCHING

It was found early on in this work that each specimen had to be heated to approximately 500 degrees Kelvin on its first heating cycle to obtain any transformation on subsequent cycles between normal transformation temperatures. This effect is due to the stabilization of the martensite phase caused by quenching in a medium at a temperature below  $M_s$  and is explained in detail elsewhere.<sup>1</sup>

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<sup>1</sup>Cook, J. M., PhD Thesis, Cambridge University, 1980.

#### IV. CONCLUSIONS

1. The effect of grain size on the martensitic transformation in Cu-Zn-Al alloys is one of stabilization of martensite (i.e. increase in  $M_s$ ) with increasing grain diameter.
2. The proposal that the repeatability of the martensite nucleation is dependent upon a dislocation substructure, the formation of which is induced by thermal cycling, and which leads to a stabilization of  $M_s$ , is supported by this work.
3. The classical method of grain refinement by deformation followed by solution treatment is applicable to the Cu-Zn-Al alloys.

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